Renewable and Sustainable Energy Reviews 19 (2013) 82–106

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Fighting global warming by photocatalytic reduction of CO_2 using giant photocatalytic reactors

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ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form
12 October 2012
Accepted 14 October 2012
Available online 7 December 2012

Keywords:
CO_2 capture
CO_2 reduction
Photocatalysis
Photocatalytic reactor
Solar chimney power plant

ABSTRACT

Over the last decades, fighting global warming has become the most important challenge humanity has to face. Therefore technologies of carbon dioxide capture, sequestration and recycling are equally important in order to tackle the global climate change stakes. Among recycling technologies, photocatalytic processes reducing CO_2 with H_2O back to fuels or to other useful organic compounds, have the potential to be part of a renewable energy system. Indeed these processes can help to control CO_2 emissions and eventually eliminate CO_2 in excess.

This perspective paper describes a large size device, able simultaneously:

- to proceed to direct air capture (DAC) of CO_2;
- to transform part of it into useful chemicals, like hydrocarbons or syngas;
- and to produce renewable energy, thus preventing future CO_2 emissions.

Synergies between solar chimney power plants (SCPPs) and semiconductor photocatalysis in order to create giant photocatalytic reactors for artificial photosynthesis are discussed, as well as scale economies for unconventional carbon capture directly from the atmosphere.

This paper presents a carbon negative emission technology obtained by coupling SCPPs with DAC systems which allows many scale economies, and also synergies to proceed to solar-to-chemical energy-conversion process by photocatalytic reduction of atmospheric CO_2 under sunlight.

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1364-0321/$ - see front matter
http://dx.doi.org/10.1016/j.rser.2012.10.026

1. Introduction

Carbon dioxide is increasing in the atmosphere due to deforestation and to fossil fuels use in industry and transportation, manufacture of cement, building heating and cooling.

With a global radiative forcing of $1.74\ W\ m^{-2}$, CO_2 is the largest contributor among well-mixed long-lived greenhouse gases, accounting for more than 63% of the total [1].

The potential of photocatalysis to mitigate or remove almost all global warming contributors like CO_2, methane CH_4, nitrous oxide N_2O, chlorofluorocarbons (CFC-11, CFC-12 and other CFCs), tropospheric ozone O_3, minor greenhouse gases GHGs (sulfur hexafluoride SF_6 and nitrogen trifloride NF_3), and also black carbon or particulate matter [2] has been reviewed recently.

Carbon capture and storage (CCS) involves collecting and generating a highly concentrated steam of almost pure CO_2, transporting and sequestering it in order to avoid atmospheric entry and contribution to climate change. CCS covers a range of technologies and techniques that hold the promise of catching up to 90% of the future CO_2 emissions from power stations and industrial sites. Once it has been trapped, CO_2 is purified and compressed to liquid, transported – often for several hundred kilometers – and then either buried in the ocean or in a geological formation suitable for sequestration (deep saline aquifers, disused coal deposit), or used for industrial purposes like enhanced oil recovery – which consists to pump CO_2 into an oil field to help extract more fuel – or transformed into mineral carbonates. The 2005 IPCC Special Report on CCS [3] provides a full description of these technologies.

Capturing CO_2 at large point sources (flue gas at an operating coal fuel or gas fired power plant) where it is quite concentrated makes sense as the power plants and the industry emits, respectively, 41 and 17% of the CO_2 [4]; however, it does not allow the capture of the CO_2 emissions from the transportation sector (23% of the emissions) or from residential and commercial sectors (10%).

Direct air capture (DAC) of diffuse CO_2 from ambient air is complementary with CCS and can deal with all types of emissions, even past ones. Maybe DAC can even be cheaper in some cases than to upgrade and retrofit the oldest conventional pulverized coal power plants and then transport the compressed CO_2 to the storage or disposal site after building hundreds of kilometers of pipelines. Pipelines to transport the CO_2 to suitable burial sites could cost more than $1 million per mile [5].

Fig. 1a shows the CO_2 emissions repartition from the different sectors (Source IEA [4]), and Fig. 1b shows the CO_2 emissions growth from different sectors between 2000 and 2005 (source World Research Institute [6]).

Power plants do not account for all the CO_2 emissions: from cars, boats, planes and others. In order to also take into account, these diffuse CO_2 emissions DAC ideas and materials have been developed by several scientists like professors Zeman [7,8] and Lackner [9–11] from Columbia University in New York.

Probably new policy instruments will oblige new fossil power plants to install CCS. Current regulatory efforts and proposed legislation seek to reduce CO_2 as well as make CCS necessary for highly pollutant industries or power plants if they do not want to buy carbon credits on the market.

Few innovative solutions to global warming induced by CO_2 emissions have been proposed. This paper focuses in its first part on the goals of carbon capture and sequestration, storage (CCS) or transformation into useful products, in order to prevent the accumulation of CO_2 in the atmosphere by catching it and converting it back to fuels, or storing it safely and permanently. Then the second and third parts of this article discusses the interest of an unusual renewable energy device (i.e., solar chimneys power plants SCPPs) and of the synergies of performing CO_2 capture directly from air with this SCPPs as many scale economies are feasible [12]. The interest of photocatalysis and the possibility to perform the reverse reaction of fuel combustion (i.e., artificial photosynthesis) in synergy with solar light under the SCPPs is then addressed in the fourth and fifth parts of this review.

2. Direct air capture (DAC) or dilute carbon dioxide capture from the atmosphere

2.1. Rationale for DAC

The process of DAC is very similar to the CCS process from concentrated CO_2 in the flue stack of a power plant: An alkali component is needed to react with weak acidic CO_2 in order to separate it from neutral gases (nitrogen N_2 and oxygen O_2). Then a regeneration process is needed to liberate the almost pure CO_2 from the salt formed and recycle the alkali component. Compression and liquefaction of CO_2 is then performed for further transportation and underground storage.

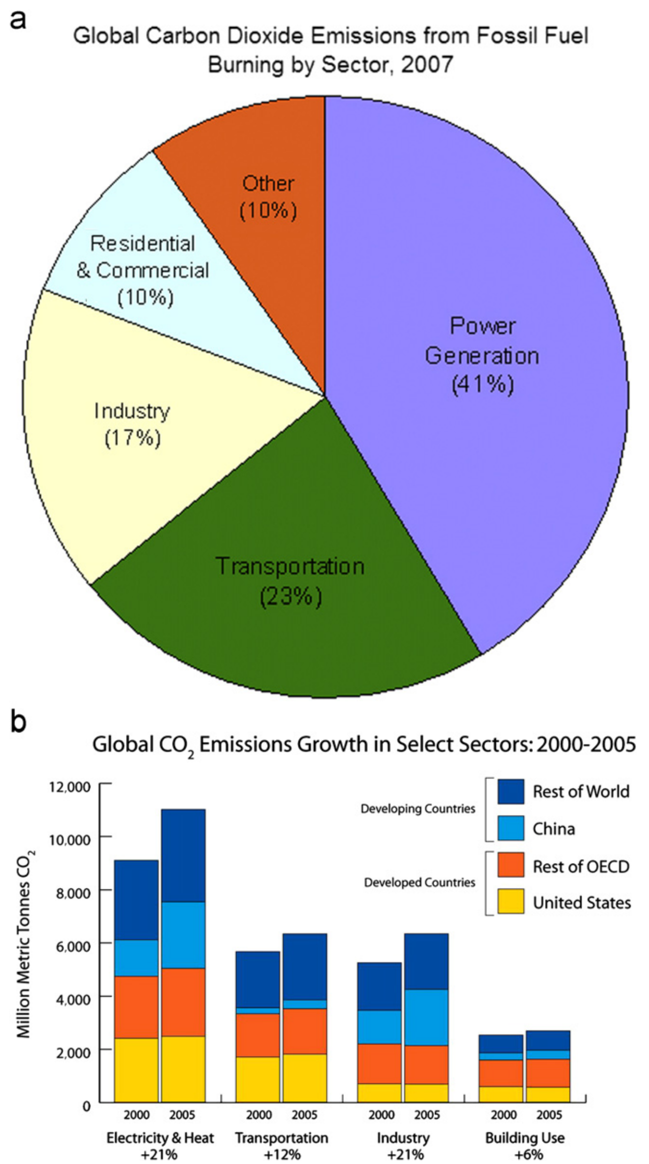


Fig. 1. (a): CO_2 emissions from different sectors (Source IEA [4]), (b): CO_2 emissions growth from different sectors (source World Research Institute [6]).
Source: IEA from international Energy Agency, "Energy-Related CO_2 Emissions by Sector in the Reference Scenario," Table 4.4, in world Energy Outlook 2009 (Paris: 2009), p. 185.

Both CCS and DAC costs can be split up into several items: initial equipment investment; CO_2 capture with sorbents; CO_2 release from sorbents; regeneration and recycling of sorbents; sorbent loss; CO_2 compression; transportation of pressurized CO_2, geological sequestration; leakage monitoring, infrastructure maintenance; environmental impacts; and others.

2.2. Comparing costs of DAC and CSS. Is the cost of air capture worth it?

The main drawback of CCS is the energy penalty caused by the CO_2 separation from other gases. It increases the CO_2 avoided cost and is an important driving force to propose new and improved capture methods with lower energy requirements. In this paper the comparison focuses on the first part of the process: The CO_2 capture, as it is assumed that some costs (compression, sequestration etc.) are identical for conventional CCS or DAC.

Recently, after a two-year study conducted by Socolow with a committee of 13 members [13,14] from academia, national or government laboratories and industry, the American Physical Society (APS) released a technical assessment stating that: "it makes little sense to ignore the emissions of CO_2 in the flue gas from a coal power plant while removing CO_2 from ambient air where it is 300 times more dilute", and that "CO_2 capture from air (air capture) will cost at least US$ 600 per ton CO_2 avoided". Therefore DAC would "play a very limited role in a coherent CO_2 mitigation strategy", as by using the same simplified costing evaluation methodology "the estimated avoided cost for 'post-combustion capture' of CO_2 from the flue gas of a reference coal power plant is about $80/t$CO_2$".

For Ranjan [15,16] "a conservative estimate for the operating cost of direct air capture came out to be $420–$630/tCO_2". This is only the cost of energy and does not take into account the capital cost of plants building. Such prohibitive mitigation costs let think that DAC cannot compete with other viable climate change mitigation options and for Ranjan cost estimates for DAC found in the literature are just not believable.

This estimates are considerably higher than the cost estimates by Keith [17,18]: $140/t CO_2, or from Stolaroff [19] for whom the cost of capturing CO_2 with a complete system would fall between 80 and 250$/t CO_2 using NaOH spray solution and he thinks this is a viable sorbent for large scale CO_2 capture. For Pielke [20], although cost assessment is not unambiguous, DAC deserves to be among the options receiving attention in the international climate policy debate. For the UK Institution of Mechanical Engineers [21], in the context of the margins of uncertainty, the costs of air capture and CCS seem to be of broadly similar magnitude.

The DAC system analyzed by the APS consisted in passing air over a solution of sodium hydroxide in a counter-current, closed system. The sodium carbonate formed is then cross-reacted with calcium hydroxide to form calcium carbonate as a precipitate. The solid calcium carbonate is then submitted to thermal decomposition with capture of the CO_2 released. The reaction scheme is [7]:

$$\text{NaOH (solution)} + CO_2 \text{ (air)} \rightarrow Na_2CO_3 \text{ (solution)} + H_2O \quad (1)$$

$$Na_2CO_3 \text{ (solution)} + Ca(OH)_2 \text{ (slurry)} \rightarrow CaCO_3 \text{ (precipitate)} + 2\ \text{NaOH (solution)} \quad (2)$$

$$CaCO_3 \text{ (solid)} + \text{heat} \rightarrow \text{CaO (solid)} + CO_2 \text{ (gas)} \quad (3)$$

$$\text{CaO (solid)} + H_2O \rightarrow Ca(OH)_2 \text{ (slurry)} \quad (4)$$

The APS report estimated that to remove CO_2 from the atmosphere as fast as a 1 GW coal plant emits it (about 6 Mt CO_2 yr^{-1}) such a system would have a total length of about 30 km (based on structures able to capture about 20 t CO_2 yr^{-1} for each square meter of frontal area, 10-m high structures, 2 m s^{-1} air flow, with CO_2 capture yield of 50%). Large quantities of construction materials (Fig. 2) and chemicals would be required and this is capital-intensive. The APS report "took into consideration a DAC with a capacity of 1 Mt CO_2/yr and estimated the capital cost to 2.2 billion dollars".

As an answer to the APS assessment [13], Climeworks [23] published a statement reminding that thermodynamics reveal that, while the CO_2 concentration differs by a factor of about 300 between flue gas and air, the minimum energy required to extract pure CO_2 differs only by a factor of about 3 [9]. According to Climeworks, their sorbent material achieves similar CO_2 loadings in an air capture process as the state of the art sorbent materials achieves for CO_2 capture from flue gases. Opposed to the reference DAC system analyzed in the APS report, their system requires more than 95% of its energy input in the form of cheap, low-temperature heat. And for the APS team the costs for DAC will not fall substantially through incremental improvements in current technology.

On the other hand Lackner [9] proposed a different technology where the energy causing the air to move through the contactor (a small part of the total energy requirement) can be provided by

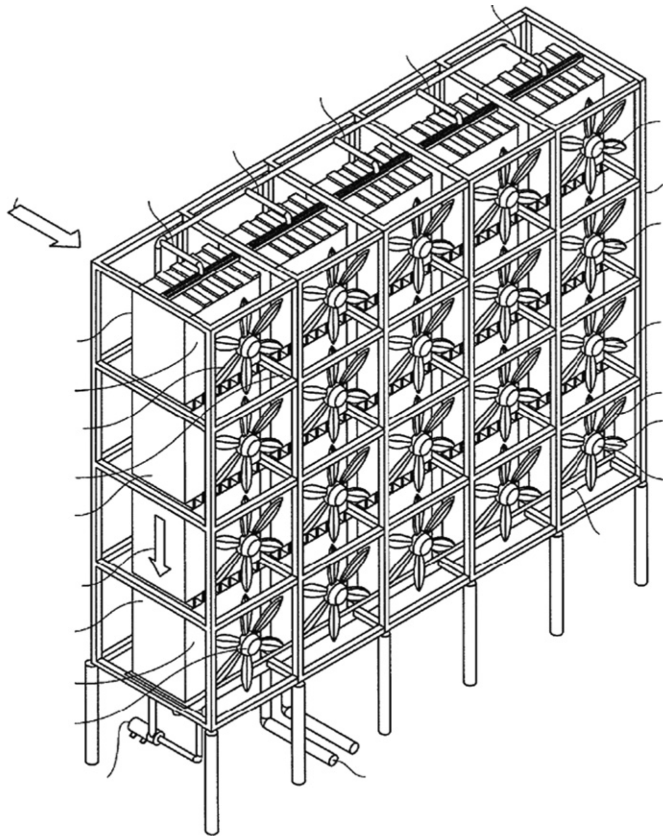


Fig. 2. Keith's DAC facility ([22] US patent 2010/0064890).

the wind. Moreover, his devices, an air capture system called "artificial or synthetic tree", uses another capture technique in which the CO_2–sorbent interaction is weak and thus the sorbent regeneration and the CO_2 release is much less energy consuming than for conventional CCS. Lackner estimates the financial cost of the technology to be \$206/t CO_2 for immediate small scale implementation; and to be around 30\$/t CO_2 after widespread mass production rollout. Indeed, the anticipated main economy of scale is based on the fall in the building costs of the units. Many other possible scale economies will be discussed later.

These "artificial trees" mimic the processes or emulate the action of natural trees by absorbing CO_2 directly from the atmosphere using solid alkaline absorbents, relying mainly on wind to perform mass transport of air across absorbent. The absorbent is then regenerated by a low temperature process, releasing almost pure CO_2, and this step represent a technological breakthrough comparatively to current CCS for the same step as it requires smaller quantities of energy.

2.3. Technical differences between DAC and CSS

Indeed, the main difference between CCS and DAC comes from the costs of CO_2 release and sorbent recycling and regeneration. For flue stack gas scrubbing, the fossil fuel power plants have to achieve a "carbon neutrality goal". For an almost zero footprint power plant, carbon capture yields need to be as quantitative as possible (commonly up to 90%), therefore currently used sorbents (generally liquid amines) bind very strongly to the CO_2, and, as a consequence, the energy required for releasing the CO_2 and regenerating the sorbent is quite important. This is the driving cost of the CSS process.

Concerning DAC, there is no carbon capture yield goal, so 30 or 40% yield can be considered as "good enough". As DAC can be done anywhere in the world, near disposal or sequestration locations, transportation of pressurized CO_2 can be reduced to minimum and there is no need to build CO_2 pipelines over long distances.

This reduced investment and transportation costs will probably give advantage to DAC over conventional CCS when regulatory constraints and binding rules will come into effect.

In the air, CO_2 is quite diluted and is a fairly inert component. How is it possible to separate it from large volumes of atmospheric nitrogen and oxygen?

Solid sorbents in the form of alkali resin polymers (commercially available for water deionization) present a permanent positive charge on which CO_2, a weak acid, can bind. The discovery by the Lackner team and his associates [24–26] that humidity can displace CO_2 from the resin, thus regenerating the sorbent, is the key of a new process referred by the authors to as "a moisture swing absorption system". Then the sorbent is dried and can again absorb CO_2 and start another DAC cycle. A first proof of the concept has been done in 2007 by the Georgia Institute of Technology and a commercial partnership called Global Thermostat [27,28]. A cost analysis has been carried out by the authors: the energy consumption for regenerating this solid sorbent represents a small part of the usual amount needed for CCS. According to Lackner and his partners, if mass production of the device was performed, costs of complete DAC could be reduced to nearly \$30/ton of CO_2 instead of the currently estimated \$100/ton with conventional CCS.

The overall process is described in Fig. 3 [29].

The plastic sheets made from dry alkaline resin are exposed to the wind flow and as air passes trough, the CO_2 loads up on the resin until almost all sites have reached the acid–base salt state. The device is then isolated in a closed regeneration chamber where the air is pumped out. Then by wetting the resin and warming it up to 40–45 °C the captured CO_2 is released, and the resin reverts to the base state. The concentrated CO_2 which has been released will be pumped out and compressed into a liquid at more or less 70 atm depending on temperature. Compression also will force the residual water vapor to condense: it is withdrawn and reused. Once the resin has dried, it can begin absorbing CO_2 again and a new cycle can start.

Energy consumption by the process machines is dominated by two steps. The first step consists in pumping the air out of the regeneration chamber. The second step, which demands far more energy, consists in compressing the CO_2 from a fraction of an atmosphere to the pressure required to liquefy it, but this step is similar to conventional CCS. According to Lackner's calculations his DAC process collects five times more CO_2 than it is generated by fossil power plants to provide its energy consumption.

Therefore the maintenance costs for DAC are reduced comparatively to CCS, as the alkali component regeneration is done under mild conditions compared to liquid amines that are warmed up to 100–140 °C in presence of numerous impurities or pollutants coming from the flue stack (NO_x, SO_x, soot, heavy metals, etc.).

A good sorbent should not only be cheap, but also should not escape from the capture system and should not be environmentally hazardous and should withstand many recycling loops. Degradation of liquid alkali sorbents requires its replacement after some cycles. Solid sorbents may be more resistant, especially if submitted to milder conditions (i.e., less corrosive pollutants and temperatures < 50 °C). Operating costs of DAC could thus be reduced comparatively to CSS, as components such as binding materials, are long lived and retain their effectiveness through a larger number of cycles.

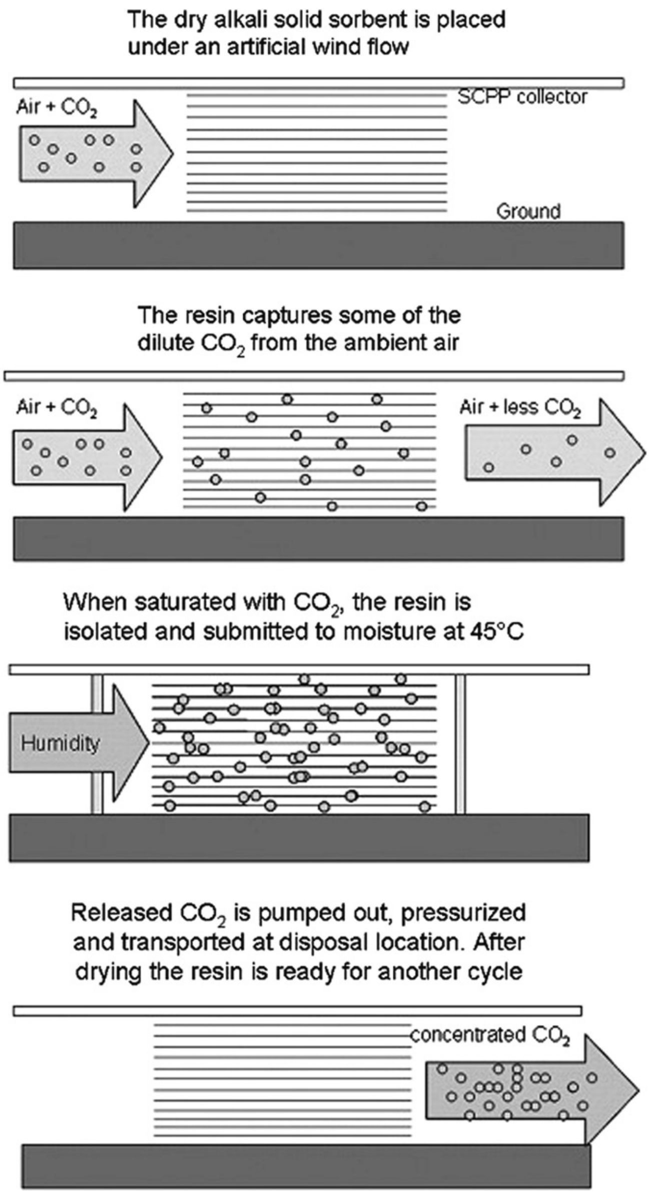


Fig. 3. Overall Lackner's DAC process (inspired from [29]).

Regardless of the discussions and controversies on the comparative costs of future CSS and DAC processes, as said by Keith [30] there is no single "cost of air capture", but rather air capture presents a potent opportunity to directly manage atmospheric CO_2 concentrations with a different set of benefits and trade-offs than other emissions mitigation options. Costs depend on design specifics, local prices of construction and energy, and on the geographic and economic niches. In this paper reducing DAC costs by at least a factor of two is explored.

3. Interest of solar chimney power plants

A solar chimney power plant (SCPP) consists of a circular greenhouse (GH) type collector with a tall chimney at its centre [31]. The air inside the transparent GH roof several meters above the ground is heated by the sun. The height of the collector increases from the exterior to the centre adjacent to the tower base. The hot air rises through the chimney by buoyancy effect where turbines produce electricity.

The SCPP is a renewable energy facility, featuring continuous power generation 24 h d^{-1} and low operation costs. The SCPP technology was experimentally tested at Manzanares in Spain, where a small prototype of 50 kW was built in 1982 and successfully tested during 7 years, by the team of Professor Schlaich [31]. The results of the operation of this demonstration plant were published by Haaf [32,33], and then by Schlaich in his 1995 book [34].

In the last decades, many researchers have carried out studies on SCPP. First, authors used thermodynamic analysis in order to study the performance of power generating system [35–37]. Later, authors focused on costs pre-estimation on large-scale SC system. Thus, Pasumarthi and Sherif [38,39] established mathematical models, based on experimental devices, describing the fluid flow and heat transfer features, while the team led by von Backström [40,41] put emphasis on turbine performance of the SCPP and Ming [42–44] set up analytical models and performed numerical simulations on turbine performance and on flow and heat transfer.

SCPPs are environmentally-friendly compared with existing coal-fired power stations and with other current renewable energy power generating technologies. For Bernardes [45] depending on the power output and on the life expectancy taken for the SCPP which can be up to more than 100 years, the environmental analysis results in, respectively approximately 170 and 70 g CO_2-equivalents/kW h for 5 and 100 MW SCPP, as with larger plants the consumption of raw materials and resources decreases. For Weinrebe [46] the greenhouse gas emissions form a 200 MW SCPP are almost similar than for wind turbine or dish sterling, almost 4 times lower than for photovoltaic's, and more than 50 times lower than for an Australian coal plant, (respectively 18, 16, 21, 84 and 980 g CO_2 equivalents/kW h). Coupled with a CSS or a DAC, SCPP becomes a "negative emissions technology", which is not the case of coal-fired power plants associated with CCS.

Moreover, contrary to other thermal power generation technologies including concentrated solar power (CSP), coal, gas and nuclear which are water intensive consumers, SCPPs do not use water for the electricity generation as they do not need any heat sink, this can be an important factor in regions with water constraints.

At the end of December 2010, the Chinese authorities [47] announced the construction of a 200 kW SCPP experimental demonstration prototype in Bay Area in Wuhai Jinsha Inner Mongolia in China [48] and the project of a 25.1 MW SCPP for 2013, accounting for desert area of 2.51 km^2 and 1.26 billion ¥ (yuan) investment. This renewed hope in the supporters' community of this unusual renewable energy, since the previous serious project dated back in the 1980s in Spain. The same happened with the multiple announcements made by the Australian company Enviromission [49]a, b] of the *La Paz solar tower project* in Arizona with the Southern California Public Power Authority Power Purchase Agreement approved in October 2010 [50] for 2014.

Several teams analysed the possibilities of building SCPPs in other places around the world, for instance Dai [51] studied the possible performance of a SCPP in the north western regions of China, Zhou [52] did the same for the Qinghai–Tibet region of China and Larbi [53] in the south western region of Algeria. Mostafa [54] estimated the performance of a solar chimney under Egyptian weather conditions and Hamdan [55] in the Arabian Gulf region. Meanwhile Ketlogetswe [56] studied the case of Bostwana, Sangi [57] did it for Iran. Nizetic [58] looked at the feasibility of implementing SCPPs in the Mediterranean region and Bilgen [59] in higher latitudes. Zhou [60] completed an exhaustive review of solar chimney power technology and also performed an economic analysis of the floating SCPP [61] idea promoted by Papageorgiou [62]a–d]. Chergui [63] analyzed the

Table 1
Typical dimensions and electricity output of different size SCPPs.

Capacity	MW	5	30	100	200
Tower height	M	550	750	1000	1000
Tower diameter	M	45	70	110	120
Collector diameter	M	1250	2900	4300	7000
Electricity output[a]	GW h yr^{-1}	14	99	320	680

[a] At a site with an annual global solar radiation of 2300 kW h m^{-2} yr^{-1}

thermo-hydrodynamic aspects and very recently Kasaeian [64] performed an experimental investigation of the climatic effects on the efficiency of a SCPP pilot prototype.

Table 1 shows the typical dimensions of SCPPS for several electricity outputs as calculated by Schlaich [31].

In order to give an example, for the ‘‘La Paz solar chimney project in Arizona’’, literature reports [65] a ‘‘4 square-mile greenhouse (10.36 km^2) directing heat toward a 2400-foot (731.5 m) tall concrete chimney’’, the total area available on the 2 Arizona sites [66] is 5500 acres (22.26 km^2) each.

For a 200 MW SCPP, with a chimney of 120 m diameter, and a wind speed of 15 m s^{-1} [34] the airflow across it is chimney is about 14.66 km^3 day^{-1} (5350 km^3 yr^{-1}). This huge airflow allows the assimilation of SCPPs to giant atmosphere vacuum cleaners.

Some authors [67] proposed SCPP variants for cleaning urban atmosphere or removing heat.

Hot air for the solar tower is produced by the greenhouse effect under the GH collector consisting of a glass or plastic glazing [68] which admits the solar radiation component and retains long-wave re-radiation from the heated ground. Thus the ground under the roof heats up and transfers its heat to the air flowing radially above it from the outside border to the tower. Due to the ground thermal storage the SCPP can operate all year round 24 h d^{-1} [69] and closed black pockets filled with water and placed on the ground act as thermal storage.

3.1. Need to couple DAC with an energy carbon neutral source

To achieve the maximum environmental benefits, the electricity needs for DAC must be obtained from carbon neutral sources. Air remediation processes using solar energy has been investigated, for instance by Von Zedtwitz-Nikulshyna [70] using CSP as the source of a high temperature process heat.

DAC processes using wind energy are mentioned by McGlashan [71]. The use of wind turbines built adjacently to a fleet of artificial trees to provide the required electric power seems interesting. Apart from savings in planning and installation costs, there are some benefits to this configuration, but wind intermittency is a handicap and a system driven by wind must operate not only intermittently but with a very low pressure drop through the contactor.

House [72] proposed using several other non-carbon energy sources (e.g., nuclear, geothermal, hydro power, wind power) with a different DAC concept. Any intermittent carbon-free energy source, like wind or solar thermal or solar electric power, will poorly match with DAC unless an energy storage system is included to produce baseload power.

In 2001 Lackner [73] proposed coupling another DAC technology to a ‘‘convection tower’’ that could either provide electricity or CO_2 capture. In fact the description he reported corresponds to the ‘‘energy tower’’ developed by Zaslavsky [74] of Technion Institute in Israel. This ‘‘energy tower’’ consists in spraying water inside a tall chimney were the evaporation of water cools the hot dry air, which falls down through the tower as it cools and becomes more dense, at the bottom of which a turbine drives a generator to produce electricity. A similar idea of coupling DAC with energy towers was proposed by Bonnelle [75] and de_Richter [76]. In 2011, a US patent by Eisenberger [77] mentioned a solar heating tower or chimney as a solar driven air current source to replace fans for CCS, but did not mention the synergies and scale economies that will be discussed later in this paper for SCPPs associated with DAC by artificial trees.

3.2. Optimization of plant output

In his book, Schlaich [34] indicated that double glazing the collector roof can increase annual plant output by 28.6% compared to the same plant with single glazed collector.

In order to increase the global performance of the solar chimney, several other authors [78–80] have envisioned a double glazing roof to increase the ability of the greenhouse collector to retain heat, but as the investment cost increases drastically, double-glazing is only envisioned for an area close to the chimney, where the air temperature under the collector is higher.

In his PhD thesis, Pretorius [81] found that the effect of double glazing the collector roof can increase of annual plant output up to 32.3%. Pretorius also studied the effect of double glazing only certain parts of the collector (the hottest part, near the chimney) while the rest of the collector stayed single glazed.

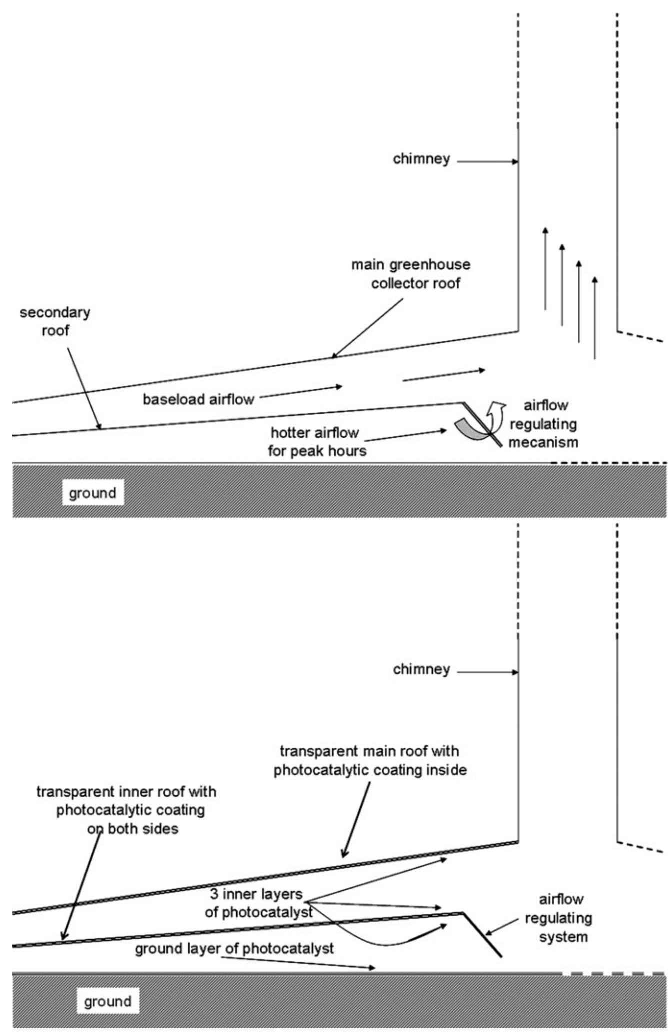


Fig. 4. SCPP with inner secondary roof to increase power output, proposed by Pretorius [81] and the possibility of adding 4 layers of photocatalytic coating (on the ground, on the inside side of the main canopy and on both sides of the inner roof).

In order to have some effective control of the SCPP output (mechanism to control the air flow through the plant), Pretorius studied the effect of a secondary roof (at 3.5 m high) (Fig. 4), and also the effect of a tertiary collector roof (at 2 m high) under the main canopy. During the sorbent regeneration process, the DAC device can play the role of this control mechanism to regulate power output.

Pretorius suggested that the air flows constantly without being regulated through the top section, while an air-flow regulating mechanism at the bottom section outlet controls the mass-flow through the bottom section of the collector. The secondary roof is expected to confer to the plant the ability to store and then release energy on demand for peak load consumption from the bottom section of the collector in order to regulate or increase the plant power output.

During base load, at times when less power is required, the bottom section is closed and energy is stored in the ground. If more power is required, the bottom section is opened in a controlled manner, which results in an extra air-flow under the secondary roof. This air-flow extracts energy from the ground and subsequently boosts plant power output. Fig. 5 illustrates schematically the operation of the plant when introducing a secondary roof.

A further refinement to achieve additional control which was considered by Pretorius is the implementation of multiple radial channels underneath the secondary roof in the collector, as illustrated by Fig. 5. These channels can be fully opened or closed off at the bottom section outlet, thereby incrementally increasing or decreasing the collector air-flow area. Papageorgiou [82] proposed a secondary modular solar collector made by a series of triangular warming air tunnels with double glazing transparent roofs.

3.3. Base load and peak load

All electrical needs for the processes: CO_2 release and sorbent regeneration, 45 °C water vapor steam, CO_2 compression, transfer and transport will be provided by the SCPP and this energy is a renewable one.

On the one hand, this local electricity consumption and also the friction losses under the greenhouse, mainly due to the CO_2 alkaline polymeric absorber (leaves of the artificial tree) and the additional equipment will decrease the overall electrical production of the power plant.

On the other hand, the CO_2 capture infrastructure (closed boxes for the regeneration process of the sorbent) will allow a better control of the electrical production during peak load when the electricity prices are much higher than during base load. The investment costs for this infrastructure is part of the DAC plant,

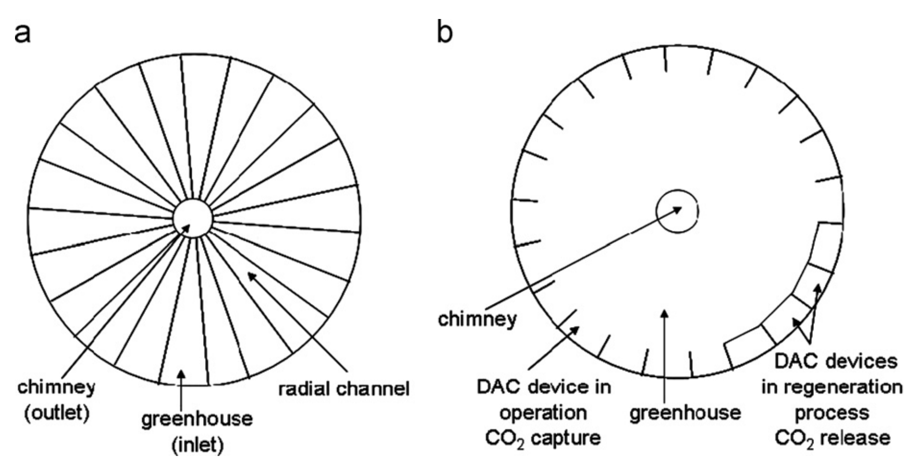


Fig. 5. (a) (left): Pretorius proposal of multiple radial channels underneath the collector: fully opened or closed off at they increase or decrease the collector air-flow area, (b) (right): similar configuration obtained with "open" or "closed" DAC devices under the canopy.

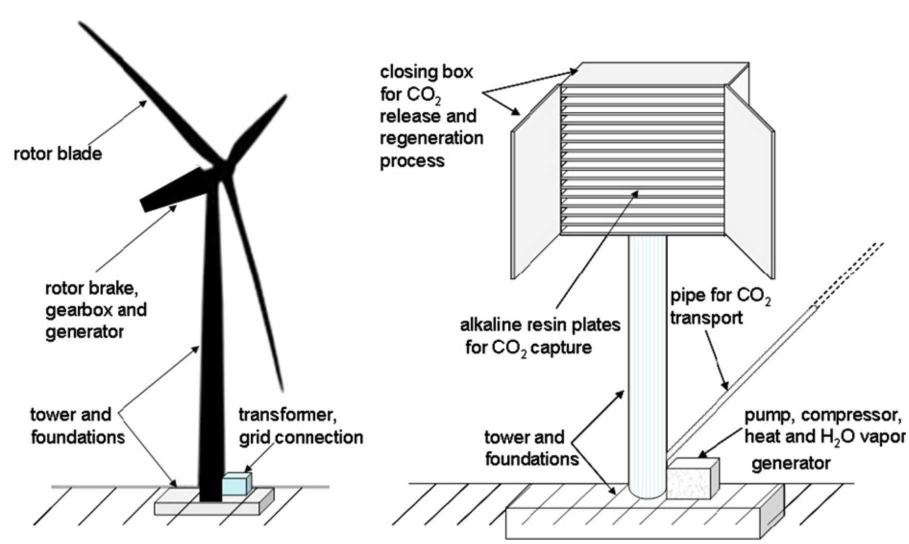


Fig. 6. Analogy between wind turbine and artificial tree.

therefore it acts in synergy with the power generation part of the plant.

4. Rationale of coupling DAC with solar chimney power plants SCPPs

CO_2 capture followed by geological sequestration or transformation associating DAC under the SCPP greenhouse allows several scale economies. In fact SCPPs operates both with solar and "artificial" wind energy and cheap energy storage allows operation 24 h d^{-1}.

Of course installing CO_2 plastic sheet scrubbers under the SCPP canopy will increase air friction and pressure drop, thus reducing power output production. Also the DAC process will consume energy, but as it will be seen later many scale economies and synergies arise from the SCPP–DAC coupling.

At a given point under the SCPP cover, the air flow and the temperature are almost constant. As seen previously the airflow for a model 200 MW SCPP with a 120 m chimney diameter and an inner wind speed of 15 m s^{-1} is about 5350 km^3 yr^{-1}. The daily CO_2 flow under this SCPP is 11,507 t; the annual CO_2 flow is 4.2 million tons. Even with only a 30% capture yield (i.e., 3452 t d^{-1} or 1.26 Mt yr^{-1}), the comparison is still interesting with the 680 GW h of renewable electricity produced in one year by the same SCPP, which allows annual savings of 0.9 million tons of CO_2 emissions [83] and provides enough electricity to about 100,000 American or Australian households.

4.1. Synergies of SCPPs coupled with DAC

In order to be submitted to an adequate wind speed, the "artificial trees" from Lackner [9] need to be quite high to reach a height where the airflow is sufficient. But even if they are located high enough, the artificial trees will operate only when wind velocity exceeds some cut-in value. Analogous rules govern the operation of wind turbines, where annually averaged wind power is typically one-third of peak wind power. Under SCPPs there is no airflow intermittency. Fig. 6 summarizes the analogies between wind turbines and artificial trees.

Although broad description of the technology is available, the early-stage proprietary nature of the work means that many details are not yet in the public domain and in particular the real costs of the different elements.

Lackner [9] has evaluated the expected financial cost to build and operate his artificial trees. He estimates that once mass production has been reached, the individual units of 500 m^2 (able to capture 10 t CO_2 d^{-1}) would cost about $20,000 each including all equipment and material comparatively to $200,000 with current technology.

The image of artificial trees [84] with trunk, stem, branches, leaves and roots is interesting to summarize ideas, but it is not so poetic and the tree trunk is expected to be the shipping container that will be used as regeneration chamber to release the captured CO_2 and regenerate the resin. It has to be equipped with some kind of engine and hydraulic cylinders for lifting and lowering the resin trays, outside or inside the chamber, respectively for carbon capture and for regeneration purposes.

In the case of wind power, 26% of the cost [85] comes from the tower and the foundations, 24% of the cost comes for gearbox and generator and nearly 50% for nacelle, machinery, rotor and blades. In the case of artificial trees, the "tree trunks" are only useful to support the active part of the device (the "leaves" made of an alkali polymeric resin). The roots (foundations) of this "synthetic trees" are also important as height and resistance to strong winds needs to be high.

The resin based CO_2 absorbent – currently a specific product – will become cheaper in the future. As the alkaline resin and its support will become cheaper, it can be anticipated that the "tree trunks" may still represent more than 25% of the investment costs even if it will depend on the eventual 'tree' design adopted. The compressors and pumps (as well as, but to a lesser extent the heat exchangers and the humidity generators) contained in each tree will become the principal capital cost as their price will not fall. Fig. 7 shows a possible implementation of the DAC under the greenhouse of a SCPP.

4.2. Scale economies of SCPPs coupled with DAC

Several obvious scale economies are thus possible under a SCPP cover:

- in order to prevent CO_2 capture devices downwind from others to process air already depleted in CO_2, by the ones upwind, all the capture units can be located in an optimum perimeter at the same distance from the centre of the SCPP collector, and all units can capture the same amount of CO_2;
- no need of high "trunk", no need of deep "roots";

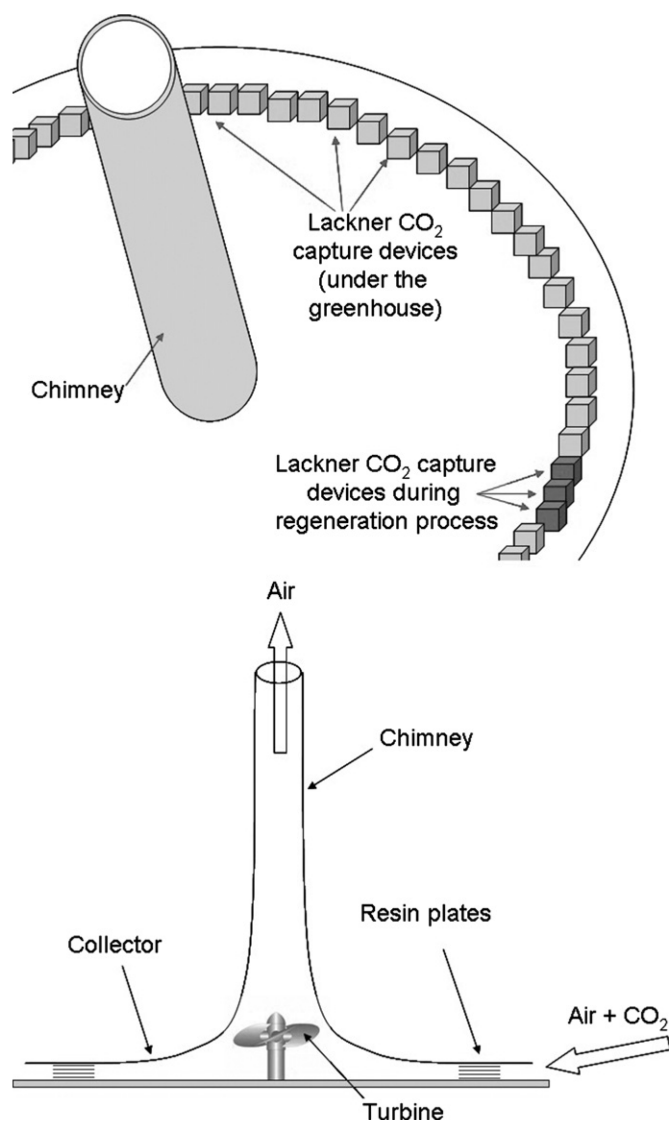


Fig. 7. Lackner CO_2 capture devices, made of alkali polymeric resin for DAC process under a SCPP cover.

- no need of engine and hydraulic cylinders for lifting and lowering the DAC devices, each unit having already four closed faces only two "doors" are needed to close the individual boxes needed for the regeneration process;
- the investment made for the regeneration chambers of the DAC process will allow the SCPP to regulate the input and output airflow: closing the air entrance during base load electricity consumption will allow the SCPP to accumulate solar heat under the canopy and in the energy storage water layer. During the peak load more power output will be obtained at a time when electricity prices are several times higher than during base load;
- shorter pipes and pipelines are needed; less infrastructure is required;
- at a given point under the SCPP GH cover the air speed, the airflow and the temperature are almost constant; under the GH there is no wind intermittency so the DAC can capture the same amount of CO_2 four times quicker than the same device submitted to natural wind;
- the SCPP collector will protect the DAC devices from heavy rains and from strong winds; operating and maintenance costs will be reduced and longer service life will be obtained: the replacement of the "trees" will be done after more years;
- more devices can be set up in a smaller area, but still collect more CO_2 in a reduced amount of time; as there is no wind intermittency and airflow speed is in the order of 3 to 4 m s^{-1}, more cycles are possible in less time; in other words, four cycles can be performed per day, and since the total area of the greenhouse opening is 44,000 m^2 (7 km diameter and at least 2 m high at the external border), nearly 3500 t of CO_2 can be captured per day with four times less resin scrubber;
- the regeneration process can be quicker (natural drying of the resin);
- the heat requested for the humidity production at 40–45 °C needed for the CO_2 release from the resin can be solar and renewable. A part of the heat can be given back to the SCPP after resin regeneration; no heating resistors needed, nor heat exchangers, as the heat requirements were planned by Lackner to be supplied from heat recovery in the CO_2 compression process;
- the heat released by the CO_2 compression step can be recycled under the SCPP;
- less compressors, less pumps, which is important as they are considered to be among the more expensive parts of the investment after the polymeric resin has entered mass production;
- reduced set up costs;
- at the locations where the devices will be installed, the support structure of the canopy collector can also be used to support the resin sorbent (the "branches, stem and leaves" of the artificial trees)
- the electricity for pumps and compressors can be renewable energy from the SCPP production;
- if energy is produced with fossil fired power plants an amount equivalent to 20% of the CO_2 captured is again released in the production of the electric power needed for the regeneration process of the sorbent. As renewable energy is used to capture CO_2 no new CO_2 emissions are made, thus the overall yield is automatically increased by 25%.

As a summary: for any given process configuration, the cycle time would ideally be as short as possible in order to maximize the utilization of installed equipment, this is the case for a DAC system under a SCPP. The SCPP investment reduces the infrastructure investment for Lakner's DAC device type, meanwhile the DAC investment allows the SCPP to produce more electricity during electric peak load consumption when selling price is higher. The SCPP locations close to CO_2 disposal or sequestration sites drastically decrease infrastructure investments for CO_2 transportation by pipelines, the DAC devices being very close to each other, pumps and compressors are shared between several, all yields are increased and there is no intermittency in any process ....

Matthews and Caldeira [86] have shown that to prevent further warming of our planet reducing CO_2 emissions to zero would not be sufficient to entail an appreciable cooling, because CO_2 already present in the atmosphere would continue to trap heat. Therefore, in order to cause a significant cooling, atmospheric greenhouse gas concentrations need to be reduced. SCPPs associated with DAC systems can at the same time provide renewable energy and remove CO_2 from the atmosphere, through a viable negative emission technology. SCPPs are robust and long lasting plants and they produce electricity at almost zero cost after the repayment of loans and capital.

4.3. Advantages of DAC under SCPPs

DAC can help mitigate emissions from small sources unsuitable for direct capture. Even old emissions can also be compensated by DAC. Lackner [9,73] explained that this technology also separates the source from disposal in a way that for instance CO_2 emissions from Europe, China or the USA can be compensated in the African Sahara desert without long distance transportation of compressed CO_2 by pipelines or without long distance shipping by boats to the disposal site.

New sorbents with better chemical kinetics and lower binding energies can substantially improve the cost of dilute CO_2 capture from ambient air, comparatively to CO_2 capture from concentrated sources in fossil carbon power plant chimneys. But solid sorbents can also be useful for conventional CCS as demonstrated by the important research efforts is this field [87–89].

4.4. Proximity of SCPPs from disposal sites

In order to minimize transport and improve the cost of the overall direct air CCS process as well as several scale economies, SCPPs can be built in the vicinity of appropriate sequestration sites like geological formations suitable for sequestration (deep saline aquifers) or close to oil wells (for enhanced oil recovery) or mining facilities.

Near abandoned and old underground coal mines are generally millions of tons of coal heaps, coal mine tailing dumps and coal slurry residues. As albedo of this waste is generally low, spread below the canopy collector of a solar chimney this waste can help accumulate heat for night electricity production.

Transforming acidic CO_2 into mineral carbonates by reaction with basalt and alkaline rocks has received extensive attention [90–93] as a way to mitigate CO_2 emissions. SCPPs can be built in locations containing this type of ultramafic ores.

Some authors [94] have proposed the production of algae biodiesel associated with solar chimneys.

Among the pros and cons, it can be argued that since the Manzanares SCPP Spanish prototype was built in the 1980s, with a 200 m tall chimney, no industrial scale SCPP with a 700 to 1000 m high chimney has been built. There is no financial or scientific interest to build intermediate prototypes with chimneys from 300 to 600 m. These prototypes would be expensive to build and the electricity produced would not be competitive if it is not subsidized. On the one hand, the fact is that even if the proof of the SCPP concept is already done and taken for granted, to be competitive with other power facilities, SCPPs need to be giant structures. On the other hand, the scientific proof of the concept

for a DAC system has also already been done by Lackner and his associates at relatively low cost, and there is no real interest to immediately build a giant DAC facility as the one proposed in this paper associated with a SCPP. The financial and industrial proof of DAC interest can follow up a classical scale up with progressive growth of costs from pilot plants to bigger and bigger prototypes. In other words, there is a financial risk to build a giant SCPP or a big DAC facility, today no one will take both risks together. But as soon as several industrial scale SCPP will be built (for instance in La Paz, Arizona, USA), installing competitive DAC systems will be possible at lower costs.

Alternative processes are needed to decrease the level of atmospheric greenhouse gases. The availability of negative emission strategies can help to meet 2 °C temperature limits.

Making negative emission strategies available will reduce the cost of keeping year 2100 CO_2 concentrations near their current level, thus planning to deploy negative emission technologies should be further considered.

4.5. *Cost reduction potential of SCPP+DAC*

The process proposed in this chapter associates a solar updraft chimney with direct air capture as a tool for emissions mitigation and fits into the portfolio of technology options for managing emissions and climate risk. In order to "fight global warming" as summarized in the title of this paper, in Sections 4 and 5 a complementary technology will focus on enabling production of transportation fuels with low carbon intensity.

In the literature plenty of data on DAC costs is available and there is a significant variance in them. An article published in 2012 by 6 scientists lead by House [95] estimates that total system costs of a DAC system will be on the order of US $1000 per tonne of CO_2, based on experience with as-built large-scale trace gas removal systems. They conclude that their "*empirical*" analyses of operating commercial processes suggest that the energetic and financial costs of capturing CO_2 from the air are likely to have been underestimated as several published analyses suggest that DAC systems may only cost a few $100/t CO_2.

As mentioned in Section 1.2, the 100 pages and two-year study of the APS conducted by Socolow and 13 scientists [14] concluded that "CO_2 capture from air (air capture) will cost US $ 600 to $800 per tonne CO_2 avoided". But the authors already cited in references [15–21] found quite different costs ranging from US $120, $250, $420, $630/t CO_2 and even $30 as a long terms goal [9]. Several sources that performed a sensitivity analysis and implied this APS report was too pessimistic in its assessment were quoted by Rudolf [96].

In response to the publication of the APS report, in a 25 pages article, Holmes [97] proved that the total costs for air contacting alone (no regeneration) can be of the order of $60 per tonne CO_2 (between $43 and $95). This estimation is based on real engineering and cost data derived from studies performed by a company named Carbon Engineering Ltd. The regeneration cycle of their process was not evaluated, as it is similar to the regeneration cycle of conventional CCS processes.

For comparative purposes, to scale up major equipment costs to full facility cost estimates Holmes [97] used similar costing methods and capital recovery factors (or even more conservative ones) than in the Socolow-APS report on DAC [14].

To explain the four fold discrepancy between their CO_2 capture costs evaluation and the evaluation performed by the APS team, they emphasize that it did not arise from differences in costing methodology, but from the APS's choice of a design, and in the operating differences of the principal parameters issued from the sensitivity analysis. For both Socolow and Holmes, a detailed cost optimization reflects engineering experience and the sensitivity analysis showed that the most important parameters are the alkaline solutions concentration (1 or 2 M) in the absorber, the rate of CO_2 removal (50 or 80%) and the air-velocity.

Holmes performed his cost optimization on a slab geometry contactor that borrows characteristics from gas scrubbing towers commonly used in the chemical processing industry, and from cooling tower designs that are well suited to cost-effective bulk air processing. The experts who wrote the APS report studied a packed tower reference design for a contactor capturing CO_2 out of air with an estimated overall cost (for the contactor alone) of $180–240 per tonne CO_2. According to Holmes, the APS used a reference design based on closed counter-flow gas scrubber column technology, a more expensive design choice, than the 'open' contactor device derived from cooling tower technology used by him. As a matter of fact, the Socolow-APS report does itself state that such a system 'would be much less costly' (APS [14], Section 2.4), and that "the largest uncertainty in the DAC cost is the cost of the air contactor".

Holmes employs fans already commonly used in forced-draught cooling towers and for which cost and efficiency are well known. The energy cost of operating the contactor is determined by Holmes [97] from the pressure drop and a pressure–volume work term, as for him the choice of air velocity is one of the many trade-offs between capital and operating costs, as high air velocities increase energy consumption, which is a primary contributor to operating costs.

In the case of our own proposal with SCPPs, there is no need to use air-fans (no investment and no electrical consumption), as the stack effect produces a "free" air-flow with air velocities which can be adjusted in the optimal range 1 to 3 m s^{-1} as determined by Holmes.

Kulkarni [98] carried out an economic analysis to obtain a net operating cost for air capture of CO_2. His cost estimates do not include capital expenses necessary to construct or maintain the air capture units. He finds that the total energy required is dominated by the parasitic losses (sensible heat requirements of the contactor (40%) and the adsorbent (28%)) and not by the mechanical energy associated with air flow (~5%). On the basis of their analysis of factors such as source of electricity, availability of low pressure steam, and geographic location, they estimated the net operating cost of capture to be ~$100/t CO_2.

The structural cost analysis breakdown of Holmes evaluates to 19% the cost percentage of fans and labour materials. It also evaluates to 36% the structural costs for fans, pumps and absorption packing. Zeman [7] estimates at 20% the total energy requirements for air movement of DAC and 56% for calcination (thermal energy used in his type of regeneration process).

In this paper we extrapolate some of the already published reports, and use them as a calculation base for a very conservative and roughly estimate of an approximate "cost reduction potential" for some steps of the new process proposed in this paper.

To simplify the life-cycle analysis, the electricity supply needs of the Holmes process are thermally integrated with the regeneration cycle, and the CO_2 from the process is captured as part of the regeneration cycle proposed. In the proposal made in this paper, using CO_2-free renewable energy produced by the SCPPs, there is no more CO_2 to capture in order to compensate the power consumption of the fans, thus 25% more CO_2 will be captured for the same cost (see Section 3.2). If we apply this conservative cost reductions and efficiency increases to the capture part of the process, the $60 per tonne of CO_2 found by Holmes fall down to nearly $40 per tonne. The other electricity consummation costs (i.e., pumping and compressing) are not subtracted, as if the DAC process consumes electricity, the SCPP own revenue is reduced.

In the APS report, on table 2.3 the energy requirements of the absorber fans per tonne of CO_2 captured is 0.63 GJ t^{-1}, and only

0.07 GJ t^{-1} for liquid pumping. A similar potential cost reduction, although not exactly identical can be applied to the Socolow [14] evaluation. According to Desmond [99], if the process power comes from a zero emissions source, thus the cost of CO_2 avoided drops from $610/t to ~$430/t taking into account the evaluation performed in the APS report on DAC for the complete process, as the APS report estimates to 0.7 the avoided CO_2 as a fraction of CO_2 captured.

Our cost reduction potential is quite conservative, as we do not take into account the structural cost reductions provided by the SCPP structure itself, nor the capital charge factor reduction (there is no investment costs for fans), or the sensible heat provided by the greenhouse for the regeneration process.

A full CCS process [100,101] also includes: the sorbent regeneration (which is energy consuming); CO_2 transportation till disposal site (which requires high investments costs) and storage.

The scale economies and synergies already described in Section 3 when associating a SCPP and a DAC system reduce the capital cost and the contingency and further decreases the complete DAC and sequestration process.

It is not in the scope of this paper to perform a complete economic evaluation of the proposed process, but one can cite among investment reductions, the fact that when captured at a fossil power plant, the CO_2 often needs transportation over long distances, using pipelines costing over $1 million per mile [5], in expensive land areas or countries and crossing dense population areas. The installation of large pipeline networks through impassable or populated areas is expensive and poses high risks. Although the financial evaluation of increased security benefits for humans and feedstock is difficult to perform, the CO_2 catastrophe that suffocated and killed 1,700 people and 3,500 livestock in Lake Nyos nearby's on August 21, 1986 should be kept in mind.

As SCPP will be built in hot deserts, when associated with DAC the location site can be chosen strategically next to the place of further CO_2 processing, eliminating transportation needs and saving $Millions in pipeline investment and capital charge factor. For instance SCPP can be built in close proximity to suitable aquifers for geological disposal, or to oil wells to perform enhanced oil recovery [102]. These locations are often far from dense populated areas (reducing risks in case of CO_2 leaks) and the land is usually cheap.

In this Section 3, the SCPP described is associated with the Lakner DAC type process, as more numerous synergies and scale economies appear: the heat needed for the moisture swing regeneration process (45 °C) is in the range of the SCPP air-temperatures (25–70 °C) and this low temperature heat can be provided to the DAC under the SCPP greenhouse.

House [95] recognises that the 300-fold concentration difference of CO_2 in flue gas (12%) and air capture (0.04%) causes the minimum work to increase by only about a factor of three, as previously stated by Lackner [9]. Therefore, the drawbacks of the high dilution of CO_2 in the air can be compensated by other advantages of air capture. Wang [103] performed a thermodynamic analysis of several fuel synthesis methods with CO_2 captured from atmosphere and concluded that the efficiency could be increased by developing technologies with lower electricity requirements like solar energy. Wang found that compared to "the energy/exergy consumed by electrolysis, the energy/exergy penalty from CO_2 capture is insignificant".

DAC is complementary to CCS as it provides a route to manage CO_2 from the transportation sector and allows industrial economies of scale to deal with small and mobile emission sources (nearly 60% of global carbon emissions). Dealing with small and dispersed CO_2 emitters with DAC would make the CO_2 collection independent of CO_2 sources, and the atmosphere could thus been considered as a means of transporting CO_2 emissions to the site of its capture. House points out that their analyses suggest that with absent radical technological breakthroughs, air capture is unlikely to be a practical CO_2 mitigation technology and that it can only be viable (i.e., CO_2 negative) if powered by non-CO_2 emitting sources. The SCPP provides a radical technological breakthrough, is a non-CO_2 emitting source and at the same time its main goal is to produce an unusual renewable energy, with many synergies and scale economies when associated with DAC as proposed in this paper.

5. Carbon dioxide recycling or artificial photosynthesis

The stabilization of the atmospheric levels of CO_2 will require the use of carbon neutral technologies and fuels [104]. In a future carbon-constrained economy, the production of transportation fuels from sunlight, at competitive costs with petroleum-based fuels, is a formidable challenge facing chemists today. The use of CO_2 to synthesize commodity chemicals has been reviewed by Arakawa [105]. Many reviews describing several methods to convert CO_2 into fuels [106–108] or about the fixation and the transformation of CO_2 [109,110], have been published. Lackner participated to the Graves [111] article which reviews the many possible technological pathways for recycling CO_2 into fuels using renewable or nuclear energy, considering three stages—CO_2 capture, H_2O and CO_2 dissociation, and fuel synthesis. Dissociation methods include thermolysis, thermochemical cycles, electrolysis, and photoelectrolysis of CO_2 and/or H_2O.

The Lackner devices are called "artificial trees", because they can withdraw, scrub or scavenge CO_2 from the atmosphere. But in nature, plants use sunlight as energy to combine H_2O and CO_2 to form biomass. Combining carbon capture and artificial photosynthesis by photocatalysis might have some interest if synergies are possible: the "fake trees" will not appear less "synthetic" but at least it would be better than "robot trees" [112].

As energy is required to compress to high pressure the CO_2 collected by the DAC devices in order to sequester it, it is interesting to try to find if CO_2 can be used or transformed on the spot with less energy for some other purpose. Small quantities of CO_2 can be used for biodiesel production with algae or for enhanced oil recovery. Quite often the conversion of CO_2 to fuels by a photo-electro catalytic approach or by the photo-electrolysis of CO_2 are described [113,114], but this article focuses on the possibilities of conversion of CO_2 to fuels by photocatalysis, as under SCPP a huge amount of free solar energy is available and therefore synergies are possible.

5.1. Interest of photocatalysis

Photocatalysis uses photocatalysts under UV or visible light illumination to reduce or to oxidize pollutants to innocuous compounds, generally at room temperature and under atmospheric pressure. Photocatalysis is an emerging technology that has gained much attention in air and water pollution control.

Photocatalytic reaction systems collect great attention because the systems need only photons as the process source and the photo-induced chemical species have strong oxidation and reduction potential. Recent advances in visible-light-responsive photocatalysts make this technology even more attractive [2].

The ability to coat almost any surface with photoactive materials is one of the reasons why photocatalysis has quickly been implemented. A large range of applications have already been commercialized and many others are still in the research phase. Some recent commercial applications include: indoor air cleaning, process vent treatment, groundwater treatment, disinfection of hospital rooms, self-cleaning lamp covers, antifogging mirrors, etc. and at very large

scale: self-cleaning paints, self-cleaning glass, and self-cleaning coatings.

5.2. Photocatalytic reduction of carbon dioxide

Ganesh [115] presented recently a comprehensive review of literature reported on conversion of CO_2 into methanol following various routes including catalytic, thermal, biological, electrochemical and photoelectrochemical. This paragraph briefly reviews the potential application of photocatalysis to recycle CO_2 in valued chemicals by photocatalytic reduction or artificial photosynthesis, and then proposes a SCPP implementation.

The reaction scheme of the photocatalytic reduction of CO_2 is the following:

$$CO_2+H_2O+h\upsilon+\text{photocatalyst}\rightarrow\text{carboneous products}+O_2 \quad (5)$$

The reduction reaction requires first (or simultaneously) the water-splitting [116,117] to produce hydrogen which will then react with the CO_2. The photocatalytic water-splitting was first described in Nature by Fujishima and Honda in [118] and since then researchers have been investigating semiconductor systems for the production of hydrogen from water. Using renewable resources for the production of hydrogen and other fuels is attractive as a sustainable non-polluting, long term contribution to supply portable high-density energy sources.

A very complete review of the recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production has been made by Ni [119]. Recently Li [120] reviewed the current progress in fuels' generation directly driven by solar energy.

In 1987, the team of Professor Graetzel [121] reported in Nature the photo-methanation of CO_2 at room temperature and atmospheric pressure using dispersed ruthenium and ruthenium oxides loaded onto titanium dioxide (TiO_2).

Few years later, many other research teams like Anpo [122,123] described photocatalytic reduction of CO_2 with water (H_2O) on various TiO_2 catalysts at room temperature, producing methanol (CH_3OH) and carbon monoxide (CO).

Several articles from Wu [124], Roy [125], Usubharatana [126], Magesh [127], Indrakanti [128], reviewed all types of photocatalysts and methods used for photo-reduction of CO_2. The most widely used catalyst is TiO_2 and the reaction products are generally methane, or methanol. However the photocatalytic conversion of CO_2 has been studied using many types of catalysts. Kočí [129] reported an overview of the literature data from 1994 until 2007 regarding CO_2 photocatalytic reduction in the presence of TiO_2.

Kočí [130] also studied the effect of temperature, pressure and volume of reactant solution on the photocatalytic reduction of CO_2 over suspended TiO_2 in an annular batch photoreactor. The same parameters were also examined in the reviews previously quoted. Very often the CO_2 reduction is conducted over TiO_2 with water or water vapor as the reductant.

The initial step in TiO_2 photo-catalysed oxidation is believed to be the formation of both hydroxyl radicals and super oxide radical anions:

$$TiO_2+h\upsilon\rightarrow e^-+h^+ \quad (6)$$

$$H_2O+h^+\rightarrow OH^\bullet+H^+ \quad (7)$$

In the absence of oxygen, OH radical, a strong oxidant and e^-, a strong reductant, are the reactive species generated on photolysis of TiO_2 in aqueous medium. In the presence of an $OH^\bullet$ or an h^+ scavenger, it is possible to use TiO_2 for photo-reduction processes.

In presence of air:

$$O_2+e^-\rightarrow O_2^{-\bullet} \quad (8)$$

Recently, Zhang [131] selectively produced CH_4 from CO_2 on Pt-loaded TiO_2 photo-catalyst; Nasution [132] performed the synthesis of methanol from CO_2 by photocatalytic reduction over copper-doped TiO_2. Li [133] found that CO was the primary product of CO_2 reduction for TiO_2–SiO_2 photocatalysts. The addition of Cu_2O species increased the overall CO_2 conversion efficiency as well as the selectivity to CH_4, by preventing the electron–hole recombination and enhancing multi-electron reactions. The peak production rates of CO and CH_4 reached, respectively 60 and 10 μmol g^{-1} h^{-1}, for 0.5%Cu/TiO_2–SiO_2.

5.3. Experimental conditions and yields of CO_2 reduction by photocatalysis

The possible use of heterogeneous photocatalysis to produce fuels using solar energy to supply clean and renewable energy is a very attractive concept. A current research objective in this field is to develop a stable visible light-responsive photocatalysts capable of achieving water splitting and/or CO_2 reduction (artificial photosynthesis). In general, it can be achieved when a photocatalyst is modified with a suitable co-catalyst and in the past years, there has been significant progress in this area. To date, more than 100 photocatalytic systems based on metal oxides have been reported to be active for overall water splitting. According to Maeda [134] some of these oxides, consisting of early-transition-metal ions (e.g., Ti^{4+}, Nb^{5+}, and Ta^{5+}) modified by a reaction promoter such as NiO, exhibit excellent quantum yields, as high as several tens of percent, without the need for sacrificial electron donors or acceptors.

As it can be seen in Table 2, numerous photocatalysts have been developed, and some have achieved high quantum efficiencies. Now days many new photocatalysts work both in the ultraviolet and the visible light region which is the main component of the solar spectrum. At present, suitable materials with sufficiently small band gap, an appropriate band gap position and the stability necessary for practical applications are available.

5.3.1. Sequential reactions

Several authors, like Sasirekha [135] reported that hydrogen levels increase rapidly, while methane contents increase sometime after those of hydrogen H_2, formaldehyde HCHO and formic acid HCOOH and the yields of methanol increase later.

Kočí [136] studied the effects of silver doping on TiO_2 for the photocatalytic reduction of CO_2: the yields of methane were negligible during the first 8 h of irradiation in almost all cases. A substantial increase of CH_4 yield was observed after 8 h of irradiation. The highest yield of methane was observed for the 7% Ag doped TiO_2 photocatalyst. The hydrogen yields were small during the first 13 h of irradiation in all cases. After 15 h the hydrogen yields increased slowly.

Kočí reported that after several hours the yields of H_2 were two orders of magnitude higher than those of methanol CH_3OH, (respectively 130 and 1.4 μmol g^{-1} of catalyst after 16 h of irradiation). The observed order of yields (μmol g^{-1} of catalyst) order was: $H_2>CH_4>CH_3OH\geq CO$.

H_2 is generated form H_2O; CH_4 is obtained from CO_2 and H_2; probably in these experimental conditions CH_3OH is obtained by oxidation of CH_4 and thus the yields are 5 times lower than those of CH_4 (6 μmol g^{-1} of catalyst).

The irradiation wavelength and many other parameters are not yet optimized. However, all the different photocatalytic processes described in the literature and reviews quoted herein can on the one hand help to remove CO_2 from the atmosphere, but also on the other hand convert CO_2 into some useful chemicals including CH_4, H_2, CO, CH_3OH, formaldehyde, ethanol,

Table 2
Yields obtained for CO_2 reduction by photocatalysis (from selected publications).

Photocatalyst	Yield[a] μ mol h^{-1} g^{-1} of catalyst	Light source	Main product	Comments	Year Ref. author
0.5 wt% CeO_2 over TiO_2	2.75 μmol h^{-1} g^{-1} for H_2	Visible-light	Hydrogen and methane	The reaction proceeded through the photodecomposition of H_2O followed by the methanation of CO_2	1992 [138] Ogura
TiO_2 suspension in liquid CO_2	[b]0.28 μmol h^{-1} g^{-1}	> 340 nm 9.6 W cm – 2 Xe lamp	Formic acid	The yield of HCOOH reached a maximum value after 30 h irradiation and then decreased[c]	1997 [139] Kaneko
0.5% TiO_2 suspension	0.43 μmol h^{-1} g^{-1}	> 340 nm 6.2 W cm^{-2} Xe lamp	Methane	High pressure CO_2 using suspended TiO_2 powders with 2-propanol as positive hole scavenger	1998 [140] Kaneco
TiO_2 powders in supercritical CO_2 fluid	[d]1.76 μmol h^{-1} g^{-1}	> 340 nm 9.6 W cm^{-2} Xe lamp	Formic acid	At 9.0 MPa and 35 °C. The yield of HCOOH increased linearly with irradiation time until 5 h and then decreased[c] gradually until 20 h	1999 [141] Kaneco
2% Cu/TiO_2 or sol–gel TiO_2 or Degussa P25	[e]19.6 μmol h^{-1} g^{-1} 0.78 μmol h^{-1} g^{-1} 6.36 μmol h^{-1} g^{-1}, respectively	254 nm 138 μW cm^{-2} 8 W Hg lamp	Methanol	Yield was significantly increased by adding 0.2M NaOH[f] (dissolves more CO_2 than pure water). In addition, the OH^- in aqueous solution also served as a strong hole scavenger	2002 [142] Tseng
Pt-$K_2Ti_6O_{13}$	[g]32.8 μmol H_2 h^{-1} g^{-1} 5.6 μmol HCHO.h^{-1} g^{-1} 20.6 μmol HCOOH.h^{-1} g^{-1}	Concentrated sunlight between 9 h30 and 15 h30 on sunny days	Hydrogen, formic acid, formal-dehyde, methane and methanol	With concentrated sunlight the average temperature[h] was 583 K in the photoreaction cell	2003 [143] Guan
0.05% TiO_2 suspension	2.4 μmol h^{-1} g^{-1}	350 nm 4.10^{15} photons. cm^{-2} s^{-1}	Methane	Yield increase 2.5 times in presence of 0.5 M 2-propanol as positive hole scavenger	2004 [144] Dey
2% Cu/TiO_2	[i]20 μmol h^{-1} g^{-1}	254 nm Hg lamp	Methanol	Switching the irradiation from 254 to 365 nm[j] resulted in a 60 times decrease of the methanol yield	2004 [145] Tseng
ZnO or NiO or TiO_2	[k]*on average* 1500 μ mol h^{-1} g^{-1}	Mono-chromatic 355 nm pulsed laser light (8 ns pulse, repetition rate 10 Hz)	Methanol	The initial yield rate is indicated, but in these experimental conditions the yields decrease[c] after 30 min irradiation.	2004 [146] Yahaya
1.2% Cu/TiO_2	0.45 μmol h^{-1} g^{-1}	365 nm 16 W cm^{-2} Hg lamp	Methanol	1.3 bar CO_2 pressure [f] 5000 s residence time. Yield increased with light intensity[l]	2005 [147] Wu
3% CuO/TiO_2	[m]442 μmol h^{-1} g^{-1}	365 nm 6 × 10 W 2450 μW cm^{-2}	Methanol	Experiments performed in 1M $KHCO_3$ at 60 °C. At 100 °C [h] the yield is 70% higher	2005 and 2009 [148–149] Slamet
TiO_2 supported on SiO_2	[n] 40+38+31+24+2 μmol h^{-1} g^{-1} H_2, HCOOH, CH4, HCHO, CH_3OH, respectively	365 nm 1000 W Hg lamp	Hydrogen, formic acid, methane, form-aldehyde and methanol	Mixture of products representing a total of 135 μmol h^{-1} g^{-1} according to curve. From 0.1 to 1% Ru over TiO_2 gives similar results.	2006 [150] Sasirekha
Cr doped multi film layers of TiO_2	[o] 1284+211+265 μmol h^{-1} g^{-1} CO, CH_4, and C_2H_6, respectively	Xe-lamp	Carbon monoxide, methane, ethane	Maximum concentration obtained after 72 h of UV illumination[c]. 70 (wt)% Cr/Ti gives the best results	2007 and 2010 [151–154] Nishimura
TiO_2 coated on sapphire,	[p]6.4 μmol CH_4.h^{-1} g^{-1}+3 μmol H_2.h^{-1} g^{-1}	broadband 200 W Hg/Xe-lamps	Methane and hydrogen	CO and O_2 probably formed and not effectively desorbed from the catalyst surface, so possible photo-oxidation of CO back into CO_2 in the reverse reaction and thus decreasing reduction yields	2008 [155] Tan
N-doped TiO_2 nano-tubes loaded with Cu and/or Pt nano-particles	[q]6.8 μmol h^{-1} g^{-1} of a mixture of hydrocarbons	Outdoor global AM 1.5 sunlight 100 mW cm^{-2}	Methane plus C2-C6 alkanes, olefins and branched paraffins	According to the authors, this hydrocarbon yield obtained under outdoor sunlight at 44 °C [h] is at least 20 times higher than previous published reports conducted under laboratory conditions using UV illumination	2009 [156] Varghese
CdSe/Pt/TiO_2 hetero-structures	[r]0.3 μmol CH_4.h^{-1} g^{-1} and 0.01 μmol CH_3OH h^{-1} g^{-1}	$\lambda > 420$ nm 300 W Xe arc lamp	Methane, methanol and trace amounts of CO and H_2	Visible light photocatalysis. Gas phase product yields expressed in ppm.	2010 [157] C. Wang
Optical fiber NiO/$InTaO_4$	11.1 μmol h^{-1} g^{-1} at 25 °C 21.0 – μmol h^{-1} g^{-1} at 75 °C 11.3 μmol h^{-1} g^{-1} at 3 PM with sunlight	λ from 400 to 1100 nm 620 nm highest intensity 327 mW cm^{-2} 100 W halogen lamp or concentrated sunlight	Methanol	[f]0.2 M NaOH solution dissolves more CO_2. The OH^- ions in aqueous solution also act as strong hole-scavengers. [i]Production rate increases with sunlight intensity (maximum reached at 3 PM). [h]Higher production rate at 75 °C than at 25 °C, possible due to the increased desorption rate of methanol	2010 [158] Z. Wang
C doped TiO_2	[s]439 μmol h^{-1} g^{-1}	Simulated daylight lamp	Formic acid	Carbon doping lowers the band gap and expends the absorption of visible light region	2011 [159] Xue

[a] In order to allow comparisons *yield written in italics* are extrapolated values with the assumption of linear kinetics curve, the original data in given forwards.
[b] 8.4 μmol g^{-1} cat after 30 h.
[c] Yield first increases then decreases, probably by secondary reactions consuming the primary products or reoxidation by the free oxygen generated.
[d] 8.8 μmol g^{-1} cat after 5 h.

(Table 2 footnote continued on next page)

[e] After 6 h: with 2.0 wt% Cu/TiO_2 methanol yield was 118 μmol g^{-1} cat, with sol–gel TiO_2 4.7 μmol g^{-1} cat and with Degussa P25 38.2 μmol g^{-1} cat.

[f] Photoreduction may be accelerated by high concentration of HCO_3^- obtained by alkali solutions that dissolves more CO_2 than does pure water, or by elevated CO_2 pressure of the reactor.

[g] With concentrated sunlight 197; 34 and 124 μmol h^{-1} g^{-1}, respectively of H_2, HCHO and HCOOH in 6 h; 408 μmol H_2 g^{-1} at ambient temperature with 150 W Hg lamp irradiation in 6 h.

[h] A simultaneous supply of photons and of thermal energy often improves the activity of photocatalysts probably because at low temperatures surface coverage is high and products do not easily desorb, thus product desorption is rate limiting.

[i] 600 μmol g^{-1} after 30 h.

[j] More efficient wavelength depending in photocatalyst bandgap.

[k] Respectively 160, 150 and 140 μmol of methanol obtained in 20 min with 300 mg of ZnO, or NiO or TiO_2 photocatalyst.

[l] Increasing light intensity increases photocatalytic yields.

[m] 2655 μmol g^{-1} after 6h at 60 °C, in the order of 4500 μmol g^{-1} after 6 h at 100 °C according to curve).

[n] According to curve.

[o] After 72 h CO, CH_4, and C_2H_6 concentrations reached, respectively 8306 ppmV (92.5 mmol g^{-1}), 1367 ppmV (15.2 mmol g^{-1}), 1712 ppmV (19.1 mmol g^{-1}).

[p] After 7.5 h: 48 μmol CH_4.g^{-1} and 22.5 μmol H_2 g^{-1}.

[q] The authors measured 5 mg carbon nano tubes for a 1 cm^2 membrane of 35 μm length, they calculated an overall hydrocarbon production rate of 160 μl h^{-1} g^{-1}, or 0.83 μl cm^{-2} h^{-1}, or 111 ppm cm^{-2} h^{-1}, and also 65 ppm H_2 ppm cm^{-2} h^{-1}.

[r] 48 and 3.3 ppm h^{-1} g^{-1}. of CH_4 and CH_3OH, respectively; if Fe used instead of Pt, H_2 production is 55 ppm h^{-1} g^{-1}.

[s] 2634 μmol g^{-1} cat after 6 h.

higher hydrocarbons, etc. providing a carbon-neutral energy alternative to fossil fuels.

But accomplishing this goal in an efficient and a cost-effective way will be challenging due to the large volumes of air that must be processed. Photocatalytic reactors can be modular and operate with negligible pressure drop. They have already been scaled up to suit a wide variety of indoor and outdoor air quality and environmental applications [137–159].

5.3.2. Temperature effect

Several authors reported that increasing the reaction temperature further increased the rate of CO_2 reduction: Anpo [160] observed that the total yields of CH_4, CH_3OH, and CO are larger at 323 K than at 275 K.

Wang [158] obtained almost a double yield of CH_3OH when increasing temperature from 25 to 75 °C. Zhang [166] obtained CH_4 yields of 0.14 and 0.115 μmol h^{-1} g^{-1} at 323 °C, and 0.56 and 0.205 μmol h^{-1} g^{-1} at 343 °C, respectively for 0.15% Pt/TiO_2 nano-tubes and 0.12% Pt/TiO_2 nano-particles (quadrupled and doubled yield depending on the catalyst). Experiments carried out by Saladin and Alxneit [161] showed that the overall reaction rate of CH_4 formation increases when the temperature rises from 25 to 200 °C. Slamet [148,149] showed an increase of methanol formation with temperature in experiments performed at 43, 60, 75 and 100 °C.

Quite often thermal energy improves the activity of photocatalysts already activated by photons, for instance when products desorption is rate limiting warming will increase the production rate, but an optimum might exist if CO_2 and reagents absorption is important. Higher temperatures might also lead to thermal catalysis, but CO_2 reduction might follow other reaction pathways, modifying selectivity.

Studying several Pt/TiO_2 photocatalysts, Yang [162] reported that all the mixtures tested showed visible light response in comparison with pure TiO_2 and also that photoproducts desorption was the rate-limiting step in the CO_2 photoreduction. Reaction products could act as electron donors for enhancing visible light hydrogen evolution from Pt/TiO_2 photocatalysts. Yang also investigated the effect of Cu dopant, pH, irradiation time and using Na_2SO_3 as a sacrificial agent.

5.3.3. Wavelength effect

Matthews [163] demonstrated that the light wavelength influences the photocatalytic yield. Tseng [145] showed that for the CO_2 reduction using TiO_2 the light with shorter wavelength (254 nm) is significantly more effective (60 times) than with 350 nm wavelength. Koci [164] observed the wavelength effect on photocatalytic reduction of CO_2 by Ag/TiO_2 photocatalyst: the main products concentrations (CH_4 and CH_3OH) were higher with the 254 nm lamp than with the 365 lamp while no products were observed with the 400 nm lamp as the catalyst was not active under visible light.

Wang [165] studied visible light photo-reduction of CO_2 using CdSe/Pt/TiO_2 catalysts; Zhang [166] demonstrated that iodine-doped TiO_2 nanoparticles are photocatalytically responsive to visible light illumination; Ogura [167] worked on a cerium oxide CeO_2_TiO_2 photocatalyst irradiated by visible light and the reaction products were H_2 and CH_4 and Varghese [156] described high rate solar photocatalytic conversion of CO_2 and water vapor to hydrocarbon fuels. Copying natural photosynthesis with photocatalytic CO_2 reduction using sunlight could be a direct method to both decrease greenhouse gases and supply sustainable energy to mankind. Thus, in order to fully harvest solar energy, visible-light driven photocatalysts are highly desired.

Recently Kin [168] demonstrated that even the NIR energy can be used as the driving source for photocatalysis besides the UV and visible energy. Improvements in the photo-efficiency of photocatalysts used in these reactions are still needed to prove feasibility, as well as scaling up the size of the photocatalytic reactors.

Efforts have to be made to extend the light absorption range of TiO_2 from UV to visible light and to NIR, and also to improve the light absorption in the overall efficiency (kg CO_2 converted kg^{-1} catalyst) as well as to increase the photocatalytic activity of TiO_2 further by adding noble metals, metal ion doping, anion doping and metal ion implantation and even the addition of sacrificial regents or newer experimental conditions to prevent backward reactions.

Table 2 gives several selected examples of CO_2 reduction experimental conditions and yields. Production rates are often expressed in terms of μmol h^{-1} g^{-1} of catalyst as the quantum yield is still low. In order to allow comparisons although the kinetics are not linear we calculated h^{-1} yields, the original data of the authors are given in the notes at the bottom of Table 2.

As seen in Table 2, the principal products are methane and/or methanol, the overall reaction schemes are:

$$CO_2+2H_2O+h\nu \leftrightarrow CH_4+2O_2 \quad (9)$$

$$CO_2+2H_2O+h\nu \leftrightarrow CH_3OH+3/2O_2 \quad (10)$$

In both cases free oxygen is a reaction product.

If CO and O_2 are formed and not effectively desorbed from the catalyst surface photo-oxidation of CO back into CO_2 in the reverse reaction is possible and thus decreases reduction yields. Secondary reactions are possible for instance leading to higher molecular-weight hydrocarbons. This explains some cases where production rates of lower molecular-weight initial products increases first and then after some time decreases or reaches a steady-state.

With excess catalyst yields can decrease, for instance in aqueous solutions when large quantity of catalyst prevents a good penetration of light in the reactor.

5.3.4. *Alkalinity effect*

With the exception of Rh/TiO_2, all these solid materials exhibit the properties of solid base catalysts; therefore the slightly acidic CO_2 can be adsorbed on the surface. The adsorption of CO_2 on the surface is particularly important since CO_2, which is a stable and linear molecular, becomes after adsorption an active specie of abundant reactivity for photocatalytic reduction. The reactors are two-phase systems and can be either gas-catalyzed or liquid-catalyzed. Generally catalyst are typically on either fluidized or fixed beds.

Adding NaOH or another alkaline solution dissolves more CO_2 than pure water, and in addition OH^- in aqueous solution also acts as a strong hole scavenger. Using organic sacrificial hole scavengers like 2-propanol decreases profitability.

In water solution the experimental results of several authors indicate that the products yields increases significantly with increasing CO_2 concentration.

The influence of water and carbonates has been studied by Dimitrijevic [169].

5.4. *Sensitivity analysis of key parameters for SCPP+photocatalysis*

Artificial photosynthetic systems are promising routes for solar-to-chemical energy-conversion process, but they are still at the laboratory stage where the principles of their assembly and functionality are still being explored. Significant challenges remain to build efficient devices capable of producing solar-fuels at a scale and at a cost that can compete with fossil fuels.

The principal interest of photocatalytic processes is mainly due to the fact that it can be powered by sunlight and that a photocatalyst like TiO_2, is usually cheap, chemically stable, available and abundant. Moreover photocatalytic reactions often occur at room-temperature and at ambient-pressure, with no need of additives or solvents. Dhakshinamoorthy [170] reviewed in 2012 the titanium containing photocatalysts, focusing on pure TiO_2 as well as on metal- and non metal-doped titania, noble metals supported on titania and micro-mesoporous titanosilicates or porous matrices containing titania clusters. Mori [171] reviewed the photocatalytic reduction of CO_2 with H_2O on various titanium oxide photocatalysts, and noted that the bulk TiO_2 powders under heterogeneous gas–solid conditions produced CH_4 as the major product, while the predominant formations of CH_3OH as well as CH_4 were observed on the highly dispersed titanium oxide moiety anchored on zeolites and mesoporous silica materials.

Photosynthetic reactions are determined primarily by three reaction processes: light-harvesting processes; charge generation and separation processes; and catalytic reaction processes (Eqs. (6)–(8)). The overall efficiency is determined by the balance of thermodynamics and kinetics of these processes. In the case of CO_2 photoreduction with water, two or more photocatalysts might be necessary, as often H_2 is generated first form H_2O; then CH_4 is obtained both from CO_2 and H_2.

As seen previously in Section 4, many types of photocatalysts and methods are used for photo-reduction of CO_2, but the synthesis of photocatalytic molecules and materials is becoming increasingly sophisticated and thus expensive. The most widely used photocatalysts are TiO_2 derivatives (Table 2) and the reaction products are generally methane, or methanol with other products [122–130].

In the scientific literature, photocatalysts are often only characterized in terms of reactivity, and selectivity, and sometimes stability but quite little is known about the cost of the photocatalysts or of their preparation.

Many parameters are important for the conversion yield, not only the size and surface area of the photocatalyst, the doping element, or the co-catalyst, but also for instance the temperature, the alkalinity and the absorption wavelength. The key parameters and driving costs were seen in previous paragraphs of Section 4.

Increasing the absorption in the visible-light region often increases the efficiency and quantum yield, but although research efforts have resulted in the emergence of new generations of visible-light-active photocatalysts, visible-light driven CO_2 reduction is at an even earlier stage of development than water splitting. On Table 2 some examples of the yields that can be obtained with selected photocatalysts are summarized. Izumi [172] reviewed in 2012 other CO_2 reduction reactions in water or with moisture using semiconductor photocatalysts other than TiO_2 (ZnO, CdS, SiC, etc) with the formation rates of the products obtained.

To understand heterogeneous photocatalytic processes, one of the keys is the surface of the active catalytic material since the chemical transformation takes place there. Consequently, the reactivity of a catalyst scales directly with the number of exposed active sites at the surface. Furthermore, photocatalysts are often doped with precious metals, and accordingly it is advantageous to disperse the photocatalytic active material as nanoparticles, not only to maximize the number of active sites and enlarge the range of wavelength reactivity, but also to keep the manufacturing cost of the catalyst low. But even if the precious metal co-catalyst is present at only 1% by weight, as the current cost of a gram of Pt, Rh or Pd is roughly a million times the cost of a gram of fuel [173] it would account for 98% of the cost of the photocatalyst. The substitution of a base metal instead of precious metals reduces the cost of the photocatalyst and makes it a possible alternative material for the purpose of an industrial application.

For a cost-effective and sustainable large-scale implementation, very different issues must be addressed and fulfilled [174], including photocatalyst cost, abundance, low toxicity and long-term stability under strong solar irradiation. These crucial requirements suggest the use of cheap transition metals and naturally abundant chemical elements such as iron, titanium, zinc, carbon, nitrogen and sulphur, and avoid using costly sacrificial agents or scavengers.

The ideal photocatalyst has a low cost and shows high performance and effectiveness, but as explained by Grills and Fujita [175], two other important parameters are turnover numbers and turnover frequencies. For a realistic system life, turnover numbers should be high and turnover frequencies should be very fast, and the current state of the art is many orders of magnitude away from either target. For each specific and individual photocatalyst, synthesized at the laboratory scale for academic research purposes, the number of possible photocatalytic cycles is yet unknown and currently it is quite difficult to extrapolate large scale production costs.

Low-cost fabrication techniques such as hydrothermal and chemical vapour deposition are now widely used, and often the active catalytic material is dispersed as nanoparticles onto high surface area supports such as silica, alumina, carbon or zeolites.

Photocatalysts anchored to cheap supports have a better chance to be developed in kilogram quantities and employed for practical applications.

Many works report the use of heterogeneous photocatalysis for deodorization and treatment of gas streams and indoor-air, and worldwide large scale use of photocatalytic self-cleaning glass, paints and coatings demonstrates the interest of photocatalysis in industrial applications, and in particular for pollution removal [**2**,176,178]. Experiments carried out in real scale showed that photocatalytic road materials induced a significant reduction in NO_x air pollutants. But further research is still strongly necessary to investigate long term performances in terms of economical vantages for the environment.

Large scale photocatalytic reduction of CO_2 to realize carbon-containing solar fuels is still in the infancy and its industrial application is still probably a decade away from making economic sense. Significant advances in efficiency are required before such devices will be able to compete with conventional energy sources. A further challenge is translating laboratory-scale academic research into scalable, industrial technologies, including considerations of large-area processing and outdoor testing [173] before large-scale implementation. Whether it is a photocatalyst for air or water purification, environmental remediation or high-density fuels production, the cost of the photocatalyst is a major factor in determining the feasibility of an application. The ideal material has a low cost and shows high performance, effectiveness and stability. Artificial photo-synthesis has the potential to provide significant economic, environmental and social benefits, providing that solar energy-conversion efficiencies increase and production/operating costs decrease. The effects of the other process variables although important practical issues appear secondary and for such large scale PCR the driving parameters will be the photocatalyst cost and lifetimes, quantum yield, visible light absorption and reaction rates.

6. Choice of experimental conditions for large scale tests of photocatalysts

As shown in Table 2, with an increase of the yields by almost three orders of magnitude, in several reduction products, this last 20 years of research has performed remarkable progress.

Several large scale tests of photocatalysis for air purification have been performed around the world. Many experiments in Europe, Japan, Hong Kong and in the USA are reported in one recent review [2].

At least 50,000 m^2 of surface area in Japan has been coated with TiO_2, and Mo [177] reports that the daily removal rate goes from 0.5 to 1.5 mmol m^{-2} and that the photocatalytic material can maintain its effectiveness with very little performance deterioration. In many cities in Japan TiO_2 has been applied in coatings, such as in Osaka, Chiba, Chigasaki, Suitama and Shinatoshin.

In Japan, Ibusuki [178] carried out tests in a roadside of a 6 lanes bound highway in Tokyo with an average traffic of 113,000 vehicles a day. Volatile organic compounds VOCs and sulfur dioxide SO_2 were, respectively removed by 17–20% and by 67–78%. The average removal percentage for nitrogen oxides NO_x with windowed panels was 31–69% during the field tests with an estimated rate of removal of 3 mmol m^{-2} d^{-1}, and the capacity of the photocatalytic sheet for NO_x removal was 20 mmol m^{-2}.

But, despite these large scale experiments on heterogeneous photocatalytic destruction of gaseous pollutants (NO_x, VOCs) and also several pilot-scale photoreactor testing [179–181] for water purification, more research is still needed and the road will be long before the challenge of producing CO_2-free fuel by direct conversion of solar energy into chemical energy is reached.

In order to make this process economically feasible, significant improvements such as the specific rate of CO_2 reduction and the quantum yield of photoreaction are needed prior to up scaling [182].

Recent work from Takeda [183] led to the discovery of a rhenium(I) complex with a very high quantum yield (0.59) for an efficient photocatalytic CO_2 reduction into CO. But large scale use and production of this expensive catalyst seems unrealistic, in the same manner as using sapphire [155] or nano-tubes [156].

This paper does not treat of photo-electro catalysis, but we report the work of Ichikawa and Doi [184,185] who explored the hydrogen production from water and the conversion of CO_2 to useful chemicals by room temperature photo-electro catalysis. A TiO_2 anatase sample tested in a single photo-electro catalysis cell unit produced hydrogen at rates of 0.42 1 h^{-1} m^{-2} (19 mmol H_2 h^{-1} m^{-2} of irradiated photocatalyst area) under sunlight without applied voltage bias and also hydrogen at a rate of 26 1 h^{-1} m^{-2} with bias under 500 W mercury lamp. We can calculate that if the photocatalyst area under a SCPP is of 1 km^2, on a sunny day, without applied voltage bias, the hydrogen evolution rate will only be approximately of 450 kg H_2 d^{-1} km^{-2}, and with bias the H_2 production can be as high as 27.8 t d^{-1} km^{-2}. But applying a voltage to 1 km^2 of photo-electrodes seems tricky.

Although some research work led to very good results at the laboratory scale, large scale application seems difficult for several reasons.

For instance, Yahaya [186] described the selective laser enhanced photocatalytic conversion of CO_2 into methanol. Optimum yield is obtained in just 20 min and is quite high. But in order to find synergies with SCPPs, sunlight has to be preferred to artificial pulsed laser light.

In experiments conducted by Wang [158] the quantum efficiency of optical-fiber reactor was found to be 14 times higher than that of the aqueous-phase reactor, because photocatalyst film on fiber had superior light-energy utilization. According to Wang and also to Wu [187], optical-fiber reactors can solve the difficulty of photon-energy delivery, as they provide a medium to transmit light uniformly throughout the reactor, especially for large-scale design. But a reactor with several km^2 of optical fiber is questionable.

A more pragmatic approach could be that of Nishimura [151,152]. In order to increase the conversion yields, they proposed a Cr doped multilayer of TiO_2 films, coated on a Cu substrate by a sol–gel and dip-coating technique. The number of film layers tested was 1, 3, 7, and 11. Also, Pathak [188,189] proposed to increase the quantity of photocatalysts for the reaction by stacking conveniently several catalytic films (Fig. 8). TiO_2 nano-particles embedded in Nafion membrane films (as in Fig. 8) could be coated with silver without neither changing the particle dispersion, nor the optical transparency of the catalytic films.

According to the authors, the translucent Nafion membrane films present a major advantage which is their photostability, as the films exhibited no deterioration in photocatalytic activities over an extended photoirradiation time (at least 50 h) and also as

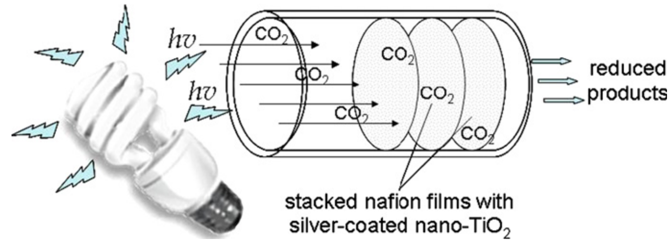


Fig. 8. Tubular reactor with several layers of transparent photocatalytic films stacked together according to Pathak [188,189].

after being washed thoroughly with deionized water, they were reusable several times with similar photoreduction results in repeated photoreduction reactions of CO_2.

The same coating methods may be used in the preparation of other metal-coated semiconductor nano-particles homogeneously dispersed in optically transparent ionomer membrane films for photocatalysis applications.

A tubular type PCR can also be envisioned for CO_2 reduction under a SCPP. This tubular PCR resting on the ground of the SCPP, presents several advantages:

- if pressure is needed for the photocatalytic reduction of CO_2, tubular type PCRs will be resistant enough;
- if warming is necessary the PCR can be circular and even several km long with several spiral loops all around the chimney, this will also increase contact time;
- they are better suited for a continuous flow process.

At the exit of the PCRs, un-reacted CO_2 is separated from the reaction products and directed towards geological sequestration. A system of heat exchangers allows recycling heat for SCPP power generation.

In the case of reaction on the gaseous phase, obtaining alcohols or olefins should be favored to facilitate separation of gaseous reactants from liquid products. For the same reasons, when working in liquid medium, trying to obtain methane or lower gaseous hydrocarbons and hydrogen could be a good strategy, but the amount of CO_2 dissolved is pressure or pH dependent. High concentrations of HCO_3^- accelerate photoreduction, thus elevated CO_2 pressure of the reactor or highly alkaline solutions are used as they dissolve more CO_2.

6.1. Choice of the reaction type

Some authors studied the photocatalytic CO_2 reduction in the presence of hydrogen. Teramura [190] uses H_2 gas as the reductant on the photoreduction of CO_2 over a Ga_2O_3 photocatalyst. Liu [191] obtained 118.5 μmol g^{-1} h^{-1} of CH_3OH yield with $RuO_2/Cu_{0.30}Ag_{0.07}In_{0.34}Zn_{1.31}S_2$ under hydrogen effect.

In the field of water splitting, many compound oxides are known to function as an effective photocatalyst and Teramura [192] was the first to show that compounds $ATaO_3$ (A=Li, Na, K) are photocatalyst oxides candidates for the reduction of CO_2, in the presence of H_2. Under photoirradiation only CO gas was generated, the photocatalytic activity was in the order $LiTaO_3 > NaTaO_3 > KTaO_3$ and after 24 h of photoirradiation with a 200 W Hg–Xe lamp the amount of evolved CO reached 0.42 μmol g^{-1} over $LiTaO_3$. CO is generated [192] and references cited there in as a result of the photocatalytic reduction of CO_2 in the presence of H_2 or CH_4 as a reductant over ZrO_2, Rh/TiO_2, MgO and Ga_2O_3.

6.2. Choice of the reactor type

Performing the CO_2 reduction reaction in solution with suspensions or dispersions of photocatalysts (fluidized bed reactor) allows vigorous agitation but presents the disadvantage of erosion by abrasion of catalyst particles and attrition of the catalyst. Milling decreased the size of the TiO_2 particles and this led to changes in the optical properties and also in significant deterioration in their photocatalytic activities [193].

Generally, in fixed bed reactors, the fluid flow regime allows achieving high conversion per unit mass of catalyst; and the low pressure drop enables such systems to be operated at reduced operating costs. So, a realistic option would be to have an easy mass transfer i.e., reaction in the gas phase with concentrated or supercritical CO_2, and a photocatalyst as effective as possible but also cheap and readily available.

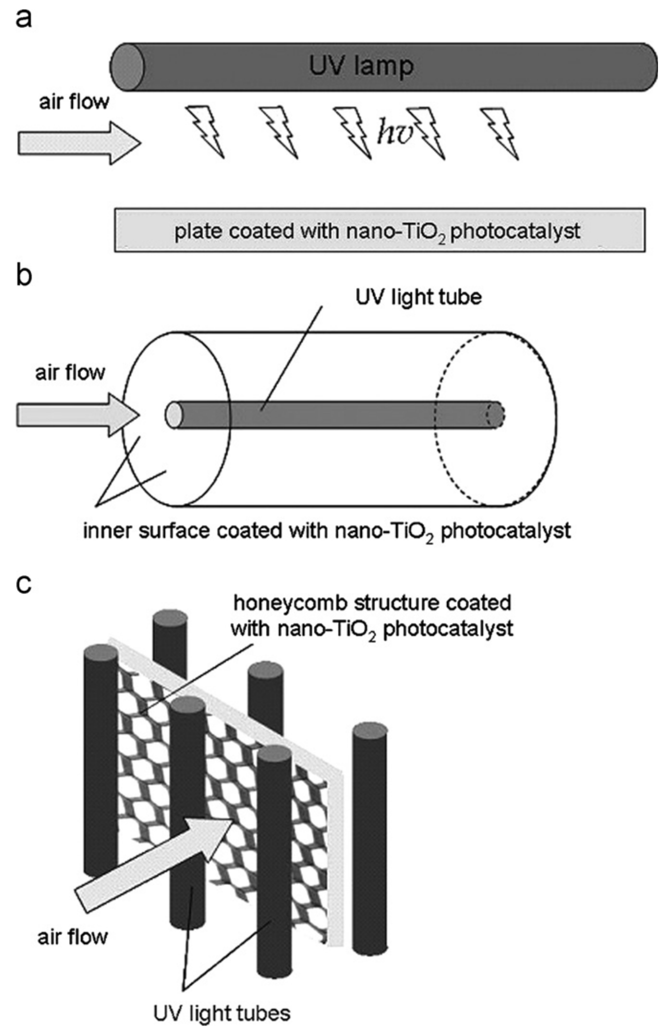


Fig. 9. Different types of PCR according to Zhang et al. [194]: (a) flat, (b) tubular and (c) honeycomb types.

Several types of photocatalytic reactors (PCR) have been developed, and they can be divided in 3 main categories [194]: plate, honey-comb or tubular as shown in Fig. 9. Among fixed-bed designs, honeycomb monoliths and annular reactors are the most common because of their higher volumes and lower pressure drops.

Kočí [195] studied recently the influence of geometry in annular batch reactors.

6.3. Research effort needed

The intrinsic idea of photocatalytic conversion of carbon dioxide and water (liquid or vapor) into hydrocarbon fuels is appealing and even if the process has historically suffered from low conversion rates, rapid advances are made as can be seen in Table 2.

The yield of photo products can be modified substantially under different experimental conditions such as light wavelengths, light intensity, sacrificial reagents or additives, temperature, reaction media, reaction time and reactor configuration. Other variables, such as CO_2 pressure, pH and oxygen and moisture content are also important in photocatalytic reduction of CO_2. But the efficiency of photocatalyst is the key parameter to a large extent. The photocatalytic reduction of CO_2 is still in its infancy. There are still many opportunities for further improvements.

Table 3
Several reactor configurations for solar photocatalytic reactions [198], Fighting global warming by photocatalytic reduction of CO_2 under giant photocatalytic reactors.

Suspended photocatalyst	Supported photocatalyst
Concentrating reactors	
Parabolic trough reactor	Parabolic trough reactor
Falling-film reactor	
Non-concentrating reactors with reflectors	
Compound parabolic collecting reactor	Tubular reactor
	Fiber-optic-cable reactor
Non-concentrating reactors without reflectors	
Flat-plate reactor	Flat-plate reactor
Trickle-down flat-plate reactor	Trickle-down flat-plate reactor
Solar pond	Thin-film fixed-bed reactor
Inflatable tube reactor	
Tubular reactors	
Pressurized tube reactor	
Double-skin sheet reactor	
Falling-film reactor	

The implementation of a photocatalytic process at an effective scale requires the use of a photo-reactor, a device which brings into contact the reactants with a photocatalyst and with light energy, as well as collecting the reaction products.

An "artificial tree" from Lackner can provide the reactants (CO_2 and H_2O vapor) with synergies and scale economies meanwhile the SCPP can provide the sunlight and the structure for the photo-reactor.

Photocatalysis offers already good prospects, but more research is needed before reaching useful giant photocatalytic reactors [75,12] able to filter several cubic kilometers of air every day, or to transform by photocatalysis several tons of products.

Intensified research effort in this direction has to be performed to:

- develop more efficient photocatalysts with enhanced photocatalytic activity and increased specificity, maybe by composite photocatalysts made of semiconductor oxides and high surface area adsorbents [196], or by molecular imprinting [197] in order to induce selectivity among the products to be photo-transformed;
- choose the best photocatalyst among the numerous candidates, which apart from cost also depend on which chemical reactions are considered and which products are expected;
- optimize the different reduction or oxidation processes, mass transport, adsorption of reagents, contact time, humidity effects, adhesion of photocatalyst to substrates, photocatalyst reactivation in case of deactivation;
- select the operating conditions, in liquid or in gaseous phase, with suspended or with supported photocatalyst;
- determine how to best organize and use photocatalytic reduction or oxidation technology;
- ensure that there are no emissions of hazardous by-products and no unexpected environmental consequences from the large scale use of these catalysts and processes;
- optimize PCR configuration, size and shape.

In Table 3 several PCR configurations are summarized according to [198,126].

6.4. Extrapolation to large scale photocatalytic reactors and photocatalytic performance

The performance and product distribution depend on the nature of the photocatalyst and the reaction conditions. Literature review shows that reactions can be carried out at room temperature and atmospheric pressure or under pressure and with water vapor. Some research teams work with CO_2-saturated aqueous solution (very diluted), some others in the gas phase or in supercritical fluid CO_2.

Best yields are often obtained after 6 to 24 h of illumination in batch reactors.

Upscaling to giant photocatalytic reactors seems difficult since many of the CO_2 reduction reactions described in the literature cited herein were generally performed in reactors with a volume $< 1\ dm^3$ and with an amount of catalysts < 1 g.

The challenge of continuous photocatalysis consists in developing PCR designs with increased efficiency, up-scalable to an industrial size. The most important parameters are: the catalyst specific area and particle size, the catalyst amount; the mass transfer rate, the flow rate, the pressure drop; the illuminated surface; the light efficiency and the intrinsic reaction kinetics.

TiO_2 is one of the most efficient photocatalysts and because of its low cost, strong oxidizing power, high stability and non-toxicity, it is already extensively used for environmental applications and complete degradation of some pollutants.

6.5. Synergies from SCPPs coupled with photocatalytic reactors

For any catalyst to be efficient, large active surface areas are needed, as well as a potent irradiation source. The SCPPs greenhouse collectors have a huge surface exposed to freely available sunlight with UV and visible-light irradiation 12 h d^{-1} and might be used as giant photocatalytic reactors (PCRs) for CO_2 mitigation by photocatalytic reduction.

The best methanol yield obtained by Slamet [148,149] for the CO_2 reduction with H_2O and copper doped TiO_2, which was of 2655 μmol g^{-1} of catalyst after 6 h of irradiation.

Thus, upscaling to the size of a SCPP and assuming that two cycles of 6 h can be performed per day (12 h sunlight) during 365 days, allows to calculate that 1.938 mol of CO_2 (85 g) could be reduced per gram of catalyst per year (0.234 g CO_2 d^{-1} g^{-1} of catalyst). In other terms, as 3452 t of CO_2 can be captured daily (nearly 1.26 Mt yr^{-1}), in order to transform back to fuels 5% of the CO_2 (173 t daily) by a solar tower with an "artificial tree", 737 t of catalyst are theoretically needed (189 m^3, as the density of TiO_2 is nearly 3900 kg m^{-3}). The projected area under the SCPP collector is of 38 km^2, if the area of photocatalyst covers 8 km^2, the amount of catalyst will be of 92 g m^{-2}. This is comparable with commercial photocatalytic coatings or paints which after application contain 50 to 100 g m^{-2} of nano-sized TiO_2. The giant photocatalytic reactor can be made of 4 double sided layers of translucent films or membranes [188,189] or multiple layers of metal doped TiO_2 films [151,152] and thus can cover only an area of 1 km^2 which gives room to install a second identical PCR and double the CO_2 transformation yield. Indeed, millions of square meters of self cleaning glasses, self-cleaning coatings, paints or cement are already in use in the world.

The rationale of PCR under the SCPP canopies comes from synergies, as the current projects for solar chimneys in Australia or Namibia forecast an area of 38 km^2 with an irradiation of more than 2200 kW h m^{-2} yr^{-1}.

A SCPP equipped with a translucent TiO_2 coated glass or polycarbonate PCR might resolve key difficulties related to the cost and to the scale-up. The shape and length of the PCR where the catalyst will be fixed can be optimized.

The SCPP provides many things a photocatalytic reactor needs:

- an external structure and an internal framework;
- a support for the PCR;
- a way to maximise the area of the photocatalyst illuminated by the light;

- an efficient illumination (no need of powerful UV lamps) natural visible light carries 10 times more energy than UV.

The rationale is that SCPPs are the only objects on earth which could be:

- in contact with the largest quantity of moving air;
- receiving huge amounts of "free" sunlight;
- being sheltered from rain and dust;
- displayed in synergy for another purpose: production of renewable electricity.

Although there are no scale economies in terms of infrastructure for a PCR, synergies are possible as the DAC Lackner device can provide CO_2 and water, and the SCPP disposes of a huge flat area and of plenty of sunlight and heat.

6.6. Improving the choice of the PCR type

A flat type PCR can be envisioned for CO_2 reduction in order to perform the photo-conversion in between the two components of double-glazing with a translucent photocatalyst inside, previously attached. But the volume inside the double glazing should not be too small.

Connection of several double-glazed panels together might raise several technical problems as the external borders must be hermetically closed and their intersection must be open to let them communicate for CO_2 introduction in one side and collection of the reduced products on the other side. For transparency as well as for cost reasons it cannot be the double glazing of the main collector roof, and therefore it should be a secondary greenhouse installed on the ground as shown in Fig. 10.

6.6.1. Contact time and radiation effect

This configuration allows the higher irradiation rate flows for both the roof and for the ground surface where the PCRs are installed. These flat PCRs as in Fig. 11 will have a radial orientation and if long contact times are needed for a high rate of photocatalytic conversion they can work by batch process.

6.6.2. Day and night overall performance

The photocatalytic CO_2 conversion into useful reduced compounds can only be done during the day under free sunlight.

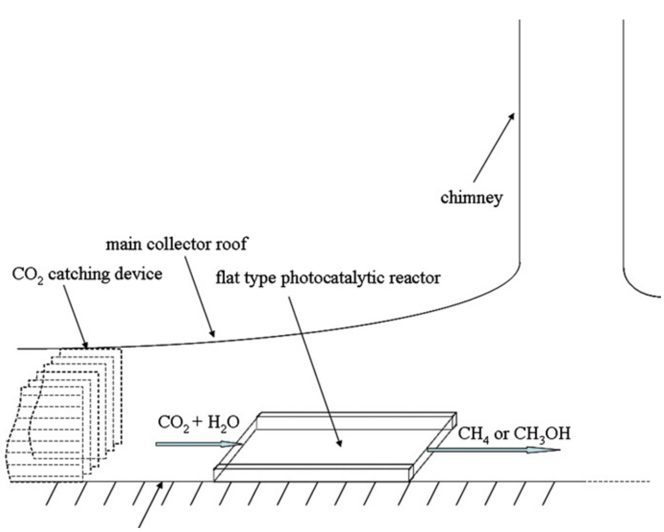


Fig. 10. Flat type photocatalytic reactor with translucent photocatalyst inside.

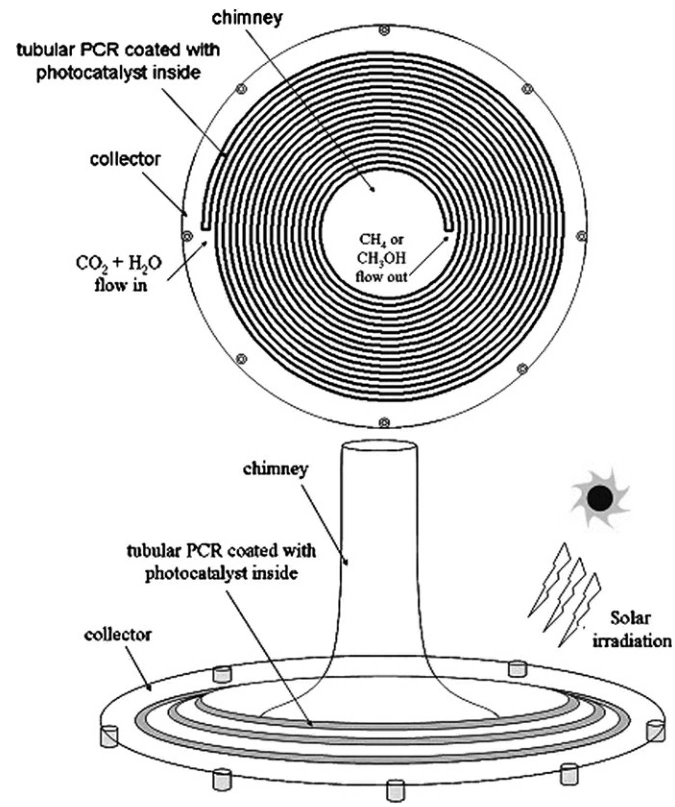


Fig. 11. Top view and lateral view of tubular type photocatalytic reactor with translucent photocatalyst inside.

Artificial lightening at night is feasible, but as there are no scale economies, only a complete financial study of the investments amortization of the infrastructure and equipment together with the yields obtained and electricity cost could help to decide if the game is worth it. So, an alternative during night is that the CO_2 captured is sequestered and stored, or sold for industrial applications like enhanced oil recovery. As the SCPPs can be built close to disposal sites, there is no need to build hundreds of km of pipelines. All waste heat of the sequestration process, for instance coming from pumps and from the compression step, can be recycled under the SCPP.

6.7. Sensitivity analysis of key parameters for photocatalytic reactors

As seen previously in this chapter during the examination of the key PCR parameters, several types of photochemical reactors are possible (Table 3) and Figs. 10 and 11 illustrate some possible implementations, but the final choice depends of the process, itself being photocatalyst dependent. Still very numerous photocatalysts can be good candidates and an infinite number of scenarios are still possible. The efficiency of currently available TiO_2-based photocatalysts is still not sufficient for practical use in fuels synthesis. Therefore, the development of new ones and optimization of existing photocatalysts exhibiting activity upon visible light with surface characteristics of improved performance and of high chemical and physical stability are crucial for broader scale utilization of photocatalytic systems in commercial applications. Once the photocatalyst and the operating conditions will be chosen, then the products obtained will fix the type of PCR and only then design specifications and costing assumptions could be formulated.

Thus, this sensitivity analysis has been limited to the identification of the most important PCO parameters as it is still premature

to try to find cost drivers and quantitative trends or to perform a cost sensitivity analysis (i.e., investment discount rate, project life-span, cost/benefits estimates ...). Many other technologies have started out at extremely high cost, which has dropped as the technology was refined and mass scale production started. Rarely the commercial viability of a young experimental technology is taken into consideration at such an early stage. The critical factors were only mentioned to better understand which parameters affect most the process of photocatalytic CO_2 reduction to fuels and photochemical systems have a long way to go to achieve their full potential and thus successfully compete with alternative approaches to produce fuels from sunlight.

7. Conclusion

Solar energy conversion systems fall into three categories according to their primary energy product: solar thermal systems, solar electricity and solar fuels. The rationale of associating SCPP and photocatalysis is that the three are gathered under the same structure. The SCPP greenhouse collects the sunlight, thermal energy is converted into artificial wind, and turbines transform kinetic energy into electricity. The photocatalytic reactor can transform the sunlight into fuels by artificial photo-synthesis using CO_2 and water. As seen in Section 3, many scale economies exist between the DAC and the SCPP, so also CO_2 could be available for in-place transformation into high density fuels. No scale economies have between described in this paper on the association of the SCPP and the PCR system, but some synergies arise from a common sheltered structure and a huge area illuminated by "free" sunlight. The availability of a renewable energy to assist in powering the plant can also reduce operating costs.

The transportation costs can be greatly reduced when the air capture and fuel synthesis devices are both constructed adjacent to renewable energy sources so an integrated process is highly desirable. Last but not least, at the final step of DAC, water removal from CO_2 might not be necessary and CO_2 compression neither, as many photocatalytic CO_2 reduction processes require water and proceed at atmospheric pressure. Sometimes increasing the temperature of photocatalytic reactions accelerates them, so the final products obtained at the end of the DAC regeneration process might be used as is.

The SCPP associated with DAC and with photocatalysis provides a radical technological breakthrough: producing a CO_2-free renewable energy and at the same time removing the principal greenhouse gas from the atmosphere and enabling production of high density transportation fuels by artificial photosynthesis. For Goeppert [199], as sunlight delivers to Earth each hour as much energy as consumed by humankind in an entire year, rather than an energy problem we have an energy collecting and storage problem. This problem could be solved by the integrated process proposed in this paper.

For Pearson [200] if CO_2 is taken from the atmosphere and transformed into energy-dense carbonaceous products, a closed-loop production process for carbon-neutral fuels is possible, improving energy independence. This process can provide chemical energy storage systems, based on the conversion of renewable energy into gaseous and/or liquid energy carriers, the latter having the higher volumetric and gravimetric energy densities. The stored energy can then either be used for power generation or in other sectors such as for transportation. Both the gaseous and the liquid fuel energy carriers are compatible with existing infrastructures and demand.

Taking into account the very large surface area submitted to sunlight radiation and occupied by SCPPs, as well as the very large daily air-flow in the chimney, it can be envisioned an optimization and synergies to address and mitigate some of the climate change consequences of global warming caused by CO_2 and other GHG.

We have shown that extensive deployment of SCPP and DAC technology capitalizing on recent scientific developments has the potential to substantially lower the risks of the anthropogenic greenhouse gases emissions.

In this paper a giant photocatalytic reactor is proposed as a device able to produce renewable electricity and at the same time capture CO_2 and transform a part of this CO_2 back into liquid fuels in order to:

- reduce some GHGs atmospheric concentration, for instance by CO_2 capture from ambient air followed by geological sequestration and/or utilization;
- provide fuels and/or useful chemicals by photocatalytic reduction of CO_2, taking profit of the very large area of the greenhouse collector canopy receiving sunlight with UV and visible-light radiation
- with minimum investment as the SCPP infrastructure can be used as the support for the PCR used for CO_2 reduction.

Alternative processes are needed to decrease the level of atmospheric greenhouse gases.

Among the technologies capable of converting solar energy, CO_2 and H_2O into easy to use fuels, there is [201] the solar thermal conversion, the combination of photovoltaic devices and electrocatalysis, or the photocatalytic conversions.

Licht proposes an original process (solar thermal electrochemical production) [202] derived for the solar generation of energetically rich chemicals like iron, aluminum, magnesium or lithium to proactively convert CO_2 into fuels. For instance, as the carbothermal iron production is responsible for 25% of worldwide industrial CO_2 emissions, Licht proposes CO_2-free production of iron by STEP. For instance, as the iron ore hematite is soluble in molten Li_2O and Li_2CO_3, Licht proposes using concentrated sunlight to heat at 650 °C molten carbonate and decrease the energy of the electrolysis reaction. Prakash [203] propose carbon capture and recycling by photocatalysts supported on silica nanosprings.

This paper presents a negative emission technology obtained by coupling SCPPs with DAC systems which allows many scale economies, and the interest of photocatalysis for the reduction of CO_2.

To enable the use of these technologies in practice, still many improvements are necessary in material optimization, as well as in reactor design and operation. But the perspective of SCPPs development is promising, as each solar chimneys power plant of 200 MW could at the same time:

- produce 680 GW h of renewable electricity per year, which is valuated as an annual saving of 0.9 million tons of CO_2 emissions [83] for every SCPP;
- deliver non intermittent renewable electricity 24 h a day, 365 days a year, with a delivered power output as constant as possible, but also that can be controlled in order to be increased during peak load and act as a peaking power facility;
- drastically reduce the investment costs of Lackner's DAC devices;
- increase the yields and drastically reducing the operational costs of DAC;
- allow negative emissions energy production;
- provide humankind with portable high-density fuels made with sunlight artificial photosynthesis by photocatalysis ....

Fuels from sunlight [204], or converting CO_2 back to fuel using solar energy is not a dream, but a challenge which still requires

long-term research to develop the application side. For the moment the yields are poor, but no matter if more free solar energy is used in recycling CO_2, than is returned by the synthetic fuels produced by recycling CO_2. "Sunlight, the original source of energy does not itself produce CO_2. As any renewable energy if it is not used it is lost anyway, but it is a lost opportunity, not a lost resource that is why we call it renewable! [205]".

As written by Centi [206,207] this project gives, "... the possibility to develop "artificial trees" able to capture the CO_2 and convert it to liquid fuels (hydrocarbons, alcohols). Therefore, the implementation of this concept will allow to reduce the levels of CO_2 in the atmosphere and at the same time capture a renewable source of energy (solar radiation) transforming it in a form (liquid fuels) which can be stored, used and transformed, preserving thus the large investments made on fossil fuels. The liquid hydrocarbons and alcohols can be alternatively used also as chemical feedstocks". Synthetic liquid hydrocarbon fuel will act as a convenient carrier of high-density energy that can be easily stored and transported.

No major changes will happen through incremental improvements, this perspective article represents a contribution to demonstrate that with the disrupting technology using together solar towers and photocatalysis, synergies are possible in order to reduce CO_2 levels in the atmosphere and at the same time produce fuels in a continuous flow photocatalytic reactor with "free" solar light. Decarbonizing at the same time the electricity sector and the transportation sector will indeed be a good transition towards a more sustainable future. Building SCPPs is really sustainable as it is a deserts energy and requires local raw materials: sand for the glass canopy and cement and iron for the chimney.

If all our energy needs (10,000 GW) were satisfied by SCPPs, the whole atmosphere would come back into one solar chimney collector every 15 years, which could help to use and reuse CO_2 indefinitely.

Since the review was submitted, several reviews on CO_2 capture form the atmosphere technologies have been published, Goeppert [199] gives a good overview. Huge progress has also been made in the CO_2 capture physisorption by metal-organic frameworks MOF. MOF is a class of stable periodic porous materials, for witch uptake and release of CO_2 is fully reversible, as is has been reviewed by Sumida [208] or McDonald [209]. Often, MOF require less energy for regeneration than systems or materials relying into chemisorption and thus are promising. Many MOF can operate under humid conditions which is an advantage compared to zeolites, which lose most of their CO_2 adsorption capacity in the presence of water.

Grills and Fujita [175] highlighted recent developments that seek to improve the efficiency of photocatalytic processes and especially CO_2 reduction with supramolecules and molecular systems in supercritical CO_2 or biphasic ionic liquid—supercritical CO_2 mixtures.

Also a long series of US patents by Eisenberger [210] were published in April and June 2012, which reviews a list of CO_2 capture and regeneration devices and techniques, and in each patent a very brief and short mention to a SCPP structure is made, but without description of the scale economies and synergies with DAC given in this paper. Another patent published in 2012 describes a DAC system disposed in circle [211], using a cooling tower.

Acknowledgments

This research work was supported in part by the National Natural Science Foundation of China (51106060).

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